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THE THEORY OF ATOMIC COLLISIONS

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PREFACE

OUR aim in this book has been to give as complete an account as possible of the application of classical and quantum mechanics to collisions between atoms, electrons, and ions. We have paid special attention to collisions between particles moving with relatively small velocities, partly because most text-books treat only the scattering of fast particles, and partly because we hope that the theory will soon be applied to problems of chemical kinetics. We have not dealt with phenomena where one of the colliding particles is a light quantum, or with problems involving a discussion of nuclear structure.

We would like to express our thanks to Dr. C. B. O. Mohr, who has helped us in the preparation of the figures, and who has read much of the book in manuscript, and to Dr. Weisskopf, for assistance in proof-reading.

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INTRODUCTION

MANY of the most important advances in physics have been due to the study of the behaviour of beams of charged particles. The researches of J. J. Thomson and others on cathode rays were responsible for the discovery of the electron and the measurement of the ratio of its charge to its mass. Similar methods enabled Kaufmann to demonstrate the relativistic variation of mass with velocity, and in the last decade the development of the method in the hands of Aston has led to our present knowledge of mass defects.

These experiments have yielded information about the nature of the charged particles themselves. Once their nature was understood, beams of charged particles have provided a most useful tool for the investigation of atomic structure. The most precise information can be obtained by bombarding matter, usually in the form of gas or a thin foil, under conditions such that very few of the incident particles make an effective collision with more than one atom. The conditions are then said to be such as to give 'single scattering'. One may then examine the energy and angular distribution of the scattered particles, or the radiation emitted by the atom.

The earliest experiment of this type was that of Rutherford, who bombarded a thin metal foil with a beam of α-particles. From the relation between the number of scattered particles and the thickness of the foil, he was able to show that the conditions were such as to give single scattering, and hence, from the variation of scattering with angle, he was led to postulate the heavy nucleus in the centre of the atom. Later developments have led to the discovery of anomalous scattering and of artificial disintegration, and have provided one of the most valuable methods of investigation of the nucleus.

Experiments in which atoms are bombarded by electrons of known energy have, in the hands of Franck, Hertz, and other workers, provided the most direct proof of the existence of the stationary states postulated by Bohr in 1913. It has been possible to measure the minimum energy required to excite the atom to a state from which it can radiate, and also to investigate the velocity distribution of the electrons after collision, and to show that scattered electrons have either lost no energy, or have lost more than the first resonance potential.

In these experiments the interest is concentrated more on the atom than on the colliding particle. It is the atom which has a planetary

structure, exists in stationary states, and radiates quanta of energy. Assuming the truth of these facts, the colliding particle behaves very much as one might expect, and provides a valuable tool for their investigation. Theoretical work has therefore, until very recently, been chiefly concerned with the stationary atomic states. This is also due to the accuracy and extent of the information about the energies of these states provided by spectroscopic methods. Early attempts were, however, made to obtain theoretical expressions for the *probability* that a colliding particle should lose energy. Thus in 1911 Bohr gave a semi-classical theory of the loss of energy of electrons and α-particles in passing through matter, from which he obtained an expression for the stopping-power which was qualitatively in agreement with experiment. Kramers in 1923 gave a theory of the emission of radiation by a particle on impact with a solid target. These formulae, while very useful as a basis with which to compare experimental results, admittedly did not rest on any secure theoretical basis.

It is one of the triumphs of the New Quantum Theory that it is able to answer questions of probability and intensity in collision problems in an unambiguous way. The first hint that classical mechanics, supplemented by quantum conditions, was inadequate in this field came from the work of Ramsauer and others, who showed that the cross-section of certain atoms in collisions with slow electrons was many times less than the gas-kinetic cross-section. But the great mass of experimental evidence is due to work carried out after the discovery of the new theory, and to some extent stimulated by it. Thus the work of Davisson and Germer and of G. P. Thomson and many others on the diffraction of electrons by crystals gives clear evidence of the wave nature of the electron. There is much experimental material concerned with the diffraction of electrons by gas atoms and molecules, most of which can be accounted for satisfactorily. There is also some evidence for the Pauli exclusion principle to be derived from collision phenomena.

The New Theory, besides accounting for these new and somewhat startling phenomena, is able to provide formulae for the stopping-power of various materials for α- and β-particles, the gas-kinetic cross-section of atoms, and many other quantities for which classical estimates have already been made. The formulae obtained from the Quantum Theory are usually in better agreement with the experiments than the older formulae, and such discrepancies as remain are probably due to the approximate mathematical methods which must be used to solve the equations, rather than to a defect in the theory itself (except in

the realm of nuclear phenomena, where the theory is known to break down).

In this book, after an introductory chapter discussing the methods of the New Quantum Theory, we shall apply these methods to problems involving collisions between material particles, and show the agreement with experiment which has been obtained.

I
THE WAVE EQUATION

1. The Wave Function

In this chapter we shall state the laws of wave mechanics, *not* in their most general form, applicable to any system however complicated, but in a simple way which can be applied only to the problem of the motion of a single charged particle in a field of force. The analysis of this chapter may also be applied to experiments in which the behaviour of a beam of electrons is investigated, provided that the interaction between the various electrons of the beam may be neglected, so that each electron behaves as though the other electrons were not there. In principle, this will of course be the case only if the charge density in the beam is vanishingly small.

We shall state the laws of wave mechanics with a view to their application to problems involving the motion of a free electron, and, since such experiments are usually carried out with beams of electrons, we shall first state the laws that describe the behaviour of steady beams.

These laws may be stated as follows: When we observe an electron, we observe a particle (a flash on a screen, a kick of a Geiger counter). If, however, we wish to know how many electrons there are likely to be in any volume, or how many cross unit area per unit time at a given point, we must assume the presence of a wave (the de Broglie wave). The amplitude and phase of this wave at a given point and given time is specified by a (complex) function of position† $\psi(x, y, z; t)$ (the wave function). This 'wave' makes its presence known to us through the following property: if $d\tau$ is an element of volume situated at the point (x, y, z), then the probability that at the instant t an electron is in the volume-element $d\tau$ is

$$|\psi(x, y, z; t)|^2 \, d\tau.$$

The average number of electrons within a volume τ large enough to contain many electrons will then be

$$\int |\psi(x, y, z; t)|^2 \, d\tau,$$

the integration being throughout the volume τ. It is to be emphasized that the probabilities refer to the results of possible experiments; $|\psi|^2 \, d\tau$ gives the probability that an electron would be found in the volume $d\tau$, if an experiment were performed to look for it.

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† (x, y, z) are Cartesian coordinates of position with respect to some axes fixed in space; t is the time coordinate.

In equation (18) we give a formula for the number of electrons crossing unit area per unit time.

We must now show how to calculate the wave function ψ that will describe correctly the behaviour of a beam of electrons in any given experiment; the method naturally depends on the kind of experiment that we have in mind. We may distinguish between two types: those in which we deal with a *steady* stream of electrons—e.g. the cathode rays in a highly evacuated discharge tube—and those in which we deal with a stream whose intensity varies with the time. The behaviour of a discharge tube when the current is first turned on presents a problem of the second type (cf. § 8).

2. Wave Mechanics of Steady Beams of Electrons

We shall first discuss the behaviour of steady streams of electrons. We shall limit ourselves in this chapter to the formulation of a non-relativistic theory, which will be valid only if the velocity of the electrons is small compared with that of light. The path of a beam of electrons is determined by the experimental conditions. If we wish to calculate the path of a beam of electrons, we must calculate ψ; $|\psi|^2$ will then be equal to the number of electrons per unit volume at any point. Thus, given the experimental conditions, it must be possible to calculate $|\psi|$ at every point.

Suppose, for instance, that a beam of electrons of known energy is passed through a slit S into a highly evacuated enclosure, where the electrons describe a curved path due to an electric field. Then it must be possible, from the experimental conditions, to calculate the function $|\psi|^2$, and, if our rules for calculating $|\psi|^2$ are correct, we must find that $|\psi|^2$ vanishes outside the region where the electrons are observed, and is equal to the observed electron density inside it.

We must first know the wave-length of the waves under these conditions. On this point we have direct experimental evidence;† the observations on the diffraction of electrons by crystals show that, if electrons are accelerated by a known potential, the wave-length λ of the associated waves is given by the formula

$$\lambda = h/\sqrt{(2mW)}, \tag{1}$$

where W is the kinetic energy of each electron. The same formula was predicted by de Broglie in 1925 from theoretical considerations.‡

W here is a directly measurable quantity, $-W/\epsilon$ being the potential

† See, for instance, G. P. Thomson, *The Wave Mechanics of Free Electrons*, Chap. IV.

‡ See, for instance, Frenkel, *Wave Mechanics*, p. 19.

drop between the source of the electrons—where they may be considered approximately at rest—and the point where the wave-length is measured. In the experiment considered above, if W_0 is the kinetic energy of the electrons when they pass the slit S, then W at any other point is given by

$$W = W_0 - V(x, y, z),$$

where $V(x, y, z)$ is the potential energy of an electron at the point (x, y, z), so that $V = -\epsilon\Phi(x, y, z)$, where Φ is the electrostatic potential difference between S and the point (x, y, z). Thus the wave-length in an experiment of this type is given at every point of space. This argument is not valid if the fields are so strong that W changes appreciably in a distance comparable with a wave-length ($\sim 10^{-8}$ cm.). Such fields are only found within the atom.

The wave-length, in a given experiment, is thus known at every point. In order to calculate the wave function, we must know also the so-called 'boundary conditions'. These depend entirely upon the experiment under consideration; in the experiment referred to above, the 'boundary conditions' consist in a knowledge of the state of the wave over the surface of the slit—i.e. the wave amplitude, wave-length, and phase. These are clearly determined by the experimental conditions, except for the phase, which can be given any arbitrary value, since it does not affect $|\psi|$; moreover, it is clear from analogies with other kinds of wave motion that, given these conditions, the wave is determined at all points of space.

In order to calculate ψ, we must know also the wave equation that it satisfies. Any monochromatic train of waves in a homogeneous isotropic medium must satisfy the equation

$$\nabla^2\psi + \frac{4\pi^2}{\lambda^2}\psi = 0,$$

where λ is the wave-length. If the medium is not homogeneous, so that λ is a function of position, the amplitude of a wave train will satisfy the same equation *approximately*, provided that the variation in λ is small in a distance comparable with λ. Putting in the experimental value of λ, namely,

$$\lambda = h/\{2m(W_0 - V)\}^{\frac{1}{2}},$$

we have for the wave equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(W_0 - V)\psi = 0, \tag{2}$$

which is the wave equation of Schrödinger.

The condition given above, that λ shall not vary much in a distance comparable with λ itself, becomes, expressed in terms of V,

$$|\mathrm{grad}\,V|\lambda \ll W. \tag{3}$$

This will clearly be satisfied for all macroscopic fields. Subject to (3), we can show that the behaviour of a beam of electrons as predicted from Schrödinger's equation is the same as that predicted by Newtonian mechanics, as follows:

If a beam of waves moves in a medium of *varying* refractive index μ, the path of the beam is curved; the radius of curvature R at any point is given by the well-known formula

$$\frac{1}{R} = -\frac{\partial}{\partial n}\log \mu.$$

Now μ is the ratio of the wave-length at the point considered to the wave-length in free space; so that in our case

$$\mu = [W_0/(W_0-V)]^{\frac{1}{2}},$$

and therefore

$$\frac{1}{R} = -\frac{\partial V}{\partial n}\bigg/ 2(W_0-V). \tag{4}$$

But, according to Newtonian mechanics, the beam will be bent in such a way that m multiplied by the acceleration v^2/R normal to path of the electrons will be equal to the component $-\partial V/\partial n$ of the external force in this direction. Substituting

$$mv^2 = 2(W_0-V)$$

we obtain (4). Thus the two systems of mechanics give the same results in this case.

We see therefore that wave mechanics will only give different results from classical mechanics when it is used to describe the behaviour of electrons in the strong fields that exist inside an atom. Before we can apply Schrödinger's equation (2) to such problems, there are two points that we must consider. Firstly, the quantity $V(x,y,z)$, the potential energy of an electron at the point (x,y,z), is no longer a quantity which can be determined experimentally. According to the uncertainty principle, if the electron is observed to be at the point (x,y,z), its velocity is unknown; and hence the change $V(x,y,z)$ in the kinetic energy as the electron travels from field-free space to (x,y,z) is not an observable quantity. Thus the only meaning that we can give to V is that it is a function which, when inserted in Schrödinger's equation, gives results in agreement with experiment. Of course, when we wish to calculate the behaviour of an electron in the field of a nucleus of charge E, our

first thought will be to use the Coulomb form of the potential

$$V(x, y, z) = -E\epsilon/r,$$

because this is the form of the potential energy of one macroscopic charged body in the field of another; but this procedure is only justified by the fact that it gives results in agreement with experiment; we have no *a priori* knowledge that this is the correct form, because $V(r)$ is not an experimentally measurable quantity.

The second point concerns the equation (2), and whether, whatever the form of V, it is the correct equation to use for atomic fields. We have seen that the equation (2), together with the probability interpretation of ψ (provided that they are applied to the behaviour of electrons in slowly varying fields), are *deductions* from the experiments on the diffraction of electrons by crystals. It is a new assumption that this equation may be applied to atomic fields. This assumption is only justified, naturally, if it gives results in agreement with experiment. The simplest test to which we can put the theory is to see whether it predicts the conservation of charge—i.e. whether it predicts that the average number of electrons going into any closed volume is equal to the number coming out of it. We shall see that this is so (§ 7).

Schrödinger's wave equation is therefore adopted because it is the simplest wave equation which gives:

(1) the de Broglie wave-length for slowly varying fields;

(2) the conservation of charge for all fields.

3. Examples of Wave Functions describing Steady Beams of Electrons. Infinite Plane Wave

A beam of electrons of infinite breadth travelling from left to right along the z-axis is represented by the wave function†

$$\psi = A \exp 2\pi i(z/\lambda - \nu t), \tag{5}$$

where λ is the wave-length, given by

$$\lambda = h/\sqrt{(2Wm)}$$

(W = kinetic energy), and ν is the frequency, given by (cf. § 8)

$$\nu = W/h.$$

The number of electrons per unit volume is AA^*, and the number per unit time crossing unit area perpendicular to the z-axis is AA^*v, where v is given by $\frac{1}{2}mv^2 = W$.

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† It is often convenient to drop the time factor and to write only $A \exp(2\pi iz/\lambda)$.

4. Beam of Electrons in Field-free Space

We suppose that the beam is formed by passing the electrons through a circular hole, of radius a, in a screen. Let us choose axes with the origin at the centre of the hole, and the axes of x and y in the plane of the screen. The direction of motion of the electrons will then be along the axis. We have to form our wave function by superimposing plane waves of wave-length λ, all travelling in directions very nearly
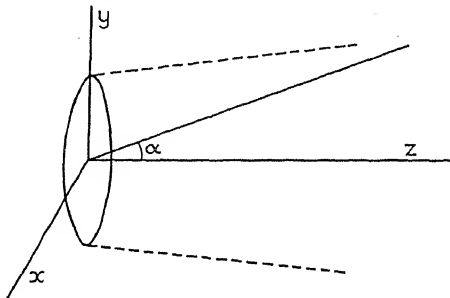
FIG. 1

parallel to the z-axis, in such a way that, in the xy-plane, ψ will vanish outside the circular hole. Now the equation of a plane wave travelling in the direction given by the polar angles† α, β is

$$A \exp\left[\frac{2\pi i}{\lambda}(z\cos\alpha + x\sin\alpha\cos\beta + y\sin\alpha\sin\beta)\right].$$

It follows that our wave function ψ must be of the form

$$\psi = \int\int A(\alpha,\beta)\exp\left[\frac{2\pi i}{\lambda}(z\cos\alpha + x\sin\alpha\cos\beta + y\sin\alpha\sin\beta)\right] d\alpha\, d\beta,$$

(6)

where $A(\alpha,\beta)$ must be chosen in such a way that ψ vanishes in the xy-plane, outside the circular aperture. If we transform to spherical polar coordinates (r,θ,ϕ) (6) becomes

$$\psi = \int\int A(\alpha,\beta)\exp\left[\frac{2\pi i}{\lambda}r\{\cos\theta\cos\alpha + \sin\theta\sin\alpha\cos(\phi-\beta)\}\right] d\alpha\, d\beta.$$

It is clear from the symmetry of the problem that A is a function of α only; carrying out the β integration we obtain

$$\psi = 2\pi \int_0^{\frac{1}{2}\pi} A(\alpha)\, d\alpha \exp\left(\frac{2\pi i r}{\lambda}\cos\theta\cos\alpha\right) J_0\left(\frac{2\pi r}{\lambda}\sin\theta\sin\alpha\right).$$

(7)

† i.e. if l, m, n are the direction cosines,

$$l = \sin\alpha\cos\beta, \qquad m = \sin\alpha\sin\beta, \qquad n = \cos\alpha.$$

To find $A(\alpha)$ we use the fact that ψ is given equal to some function $f(r)$, say, on the xy-plane, i.e. on the plane $\theta = \frac{1}{2}\pi$; we have then

$$f(r) = 2\pi \int_0^{\frac{1}{2}\pi} A(\alpha)\, d\alpha\, J_0\!\left(\frac{2\pi r}{\lambda}\sin\alpha\right). \tag{8}$$

From this integral equation $A(\alpha)$ must be determined.

The simplest convenient expression for $f(r)$ is

$$f(r) = B\exp(-r^2/a^2). \tag{9}$$

In practice $f(r)$ would be more complicated than this, being constant within the hole ($r < a$), and falling to zero in some irregular way at the boundary. We adopt the simplified form (9) because it makes possible the exact solution of (8). If we put

$$A(\alpha) = Ce^{-(\sin\alpha/\sigma)^2}\sin\alpha\cos\alpha$$

with
$$\sigma = \lambda/\pi a, \qquad C\pi\sigma^2 = B,$$

then equation (8) is satisfied† if we replace the upper limit of integration by ∞, a step which may easily be justified since $\sigma \ll 1$.

We have now to integrate (7). Since the whole value of the integral comes from small α, we replace (7) by

$$\psi = 2\pi C \int_0^\infty e^{-\alpha^2/\sigma^2}\exp\!\left[\frac{2\pi i r\cos\theta}{\lambda}(1-\tfrac{1}{2}\alpha^2)\right] J_0\!\left(\frac{2\pi r\alpha}{\lambda}\sin\theta\right)\alpha\, d\alpha,$$

which is equal to

$$\pi C\left\{\frac{1}{\sigma^2} - \frac{\pi i r\cos\theta}{\lambda}\right\}^{-1}\exp\!\left[-\frac{\pi^2 r^2}{\lambda^2}\sin^2\theta\left\{\frac{1}{\sigma^2} - \frac{\pi i r\cos\theta}{\lambda}\right\}^{-1}\right]\exp(2\pi i z/\lambda), \tag{10}$$

which is the required wave function. The number of particles per unit volume is $|\psi|^2$, which, for large r, tends to

$$(C\lambda/r)^2\exp(-2\sin^2\theta/\sigma^2),$$

which is equal to

$$|\psi|^2 \sim (\pi B a^2/\lambda r)^2\exp(-2\pi^2 a^2\sin^2\theta/\lambda^2). \tag{11}$$

The diffraction of the beam is well shown.

5. One-dimensional Problems

Let us suppose that a beam of electrons, such as the beam discussed in the last section, moving along the z-axis, enters a field which varies

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† Cf. Watson, *Theory of Bessel Functions*, p. 393. We use the formula
$$\int_0^\infty J_0(at)e^{-t^2/\sigma^2}t\, dt = \tfrac{1}{2}\sigma^2 e^{-\frac{1}{4}a^2\sigma^2}.$$

only in the z-direction, so that the potential energy of an electron in this field is of the form $V(z)$. It is required to calculate the behaviour of the beam.

In such problems the variation of ψ with x, y is not relevant; for purposes of calculation it is therefore convenient to take the incident beam of infinite extent, so that it may be represented by an infinite plane wave. The complete wave function ψ will then be a function of z only, and will therefore satisfy the wave equation

$$\frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(W-V)\psi = 0, \tag{12}$$

where W is the kinetic energy of each electron at the point where V is considered zero.

As an example,† we shall investigate the behaviour of a beam of electrons impinging on a potential jump, that is to say, a field such that

$$V = 0 \qquad (z < 0),$$
$$V = U \qquad (z > 0).$$

We shall suppose that $U < W$. We represent the incident wave, falling on the potential jump, by

$$A \exp(ikz) \qquad (z < 0),$$

where $\qquad k = 2\pi m v/h = 2\pi(2mW)^{\frac{1}{2}}/h.$

This represents a beam of electrons moving with velocity v, and such that AA^*v cross unit area per unit time. For the reflected beam we take

$$B \exp(-ikz) \qquad (z < 0),$$

and for the transmitted beam

$$C \exp(ik'z) \qquad (z > 0),$$

where $\qquad k' = 2\pi m v'/h = 2\pi[2m(W-U)]^{\frac{1}{2}}/h.$

Thus for our complete wave function we have

$$\psi = A \exp(ikz) + B \exp(-ikz) \qquad (z < 0),$$
$$\psi = C \exp(ik'z) \qquad\qquad\quad (z > 0).$$

We now put in the boundary conditions satisfied by the wave function at $z = 0$. These are that ψ and $\partial\psi/\partial z$ must be continuous. We have therefore

$$A + B = C$$
$$k(A - B) = Ck'.$$

† A discussion of the passage of electrons across potential barriers is given in various text-books. Cf. Frenkel, *Einführung in die Wellenmechanik*, pp. 52–60, and *Wave Mechanics*, § 15; Condon and Morse, *Quantum Mechanics*, pp. 222 et seq.; also in Condon, *Rev. Mod. Phys.*, **3** (1931), 43. A summary of the application of these ideas to electron emission from metals is given by Nordheim, *Phys. Zeits.*, **30** (1929), 177.

Solving, we obtain

$$B = A(k-k')/(k+k')$$
$$C = 2Ak/(k+k').$$

The number of particles crossing unit area per unit time in the reflected beam is

$$AA^*v(k-k')^2/(k+k')^2,$$

and in the transmitted beam

$$AA^*v'(2k)^2/(k+k')^2.$$

Remembering that $k/k' = v/v'$, we see that the fraction of the total number of particles reflected is

$$(v-v')^2/(v+v')^2$$

and the fraction transmitted

$$4vv'/(v+v')^2.$$

We see that the two proportions add up to unity, so that the wave function predicts that electrons are conserved. This is a particular case of a general law proved below in § 7.

6. Solution of the Wave Equation for an Electron in a Slowly Varying Field†

If the potential energy $V(z)$ does not vary appreciably in a distance comparable with the wave-length $h/\sqrt{\{2m(W-V)\}}$, one may obtain an approximate solution of the wave equation as follows. We write

$$\frac{8\pi^2 m}{h^2}(W-V) = f(z),$$

and assume $f(z)$ positive in the range of z considered. Schrödinger's equation becomes

$$\frac{d^2\psi}{dz^2} + f(z)\psi = 0. \tag{13}$$

We write
$$\psi = Ae^{i\beta}; \tag{14}$$

substituting into (13) we obtain

$$A'' + 2iA'\beta' + i\beta''A - \beta'^2A + fA = 0, \tag{15}$$

where the dashes denote differentiation with respect to z. We put

$$\beta'^2 = f(z),$$

which gives

$$\beta = \int^z [f(z)]^{\frac{1}{2}}\, dz.$$

Since f is nearly a constant in a range of z long compared with the wave-

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† This method is due to Jeffreys, *Proc. Lond. Math. Soc.*, Ser. 2, **23**, Part 6.

length, this gives for β in such a range,

$$\beta \simeq f^{\frac{1}{2}}z + \text{const.}$$

It follows from (14) that A to a first approximation is constant in such a range, and hence that

$$A'' \ll A'f^{\frac{1}{2}} \ll Af.$$

Hence in (15) we may neglect A'' in comparison with $A'\beta'$ [we cannot neglect $A'\beta'$ in comparison with $A\beta''$ because β'' is itself small]. We thus obtain from (15)

$$2A'\beta' + \beta''A = 0,$$

and hence $A = \text{const.}[f(z)]^{-\frac{1}{4}}.$

Thus our approximate solution is

$$\psi = [f(z)]^{-\frac{1}{4}}\exp\left\{\pm i \int\limits^{z} [f(z)]^{\frac{1}{2}}\, dz\right\}. \tag{16}$$

The number N of electrons crossing unit area per unit time is equal to $|\psi|^2$ multiplied by the velocity of the electrons. Now

$$|\psi|^2 = [f(z)]^{-\frac{1}{2}}$$

and the velocity of the electrons is $[2(W-V)/m]^{\frac{1}{2}}$, which is proportional to $[f(z)]^{\frac{1}{2}}$. Thus N is the same for all z, as it should be.

Similarly, it may be shown that, if $f(z)$ is negative, then, if we write

$$g(z) = -f(z) = \frac{8\pi^2 m}{h^2}(V-W),$$

the approximate solutions of the wave equation (13) are

$$[g(z)]^{-\frac{1}{4}}\exp\left\{\mp \int\limits^{z} [g(z)]^{\frac{1}{2}}\, dz\right\}.$$

In many problems $f(z)$ has a zero z_0 such that

$$f(z) > 0 \qquad (z > z_0)$$
$$f(z) < 0 \qquad (z < z_0),$$

and we require to know the particular solution which *decreases* as z becomes less than z_0. It has been shown by Jeffreys† that, if $f'(z_0) \neq 0$, then in the range $z > z_0$ this solution is

$$\psi = f^{-\frac{1}{4}}\sin\left[\tfrac{1}{4}\pi + \int\limits_{z_0}^{z} [f(z)]^{\frac{1}{2}}\, dz\right]. \tag{17}$$

7. Formulae for the Current; the Conservation of Charge

We have postulated as an axiom that the quantity $\psi\psi^*$ shall be equal to the number of electrons per unit volume in the beam of electrons

† Loc. cit.

described by the wave function ψ, or more exactly, that $\psi\psi^* \, d\tau$ is equal to the probability that an electron will be found in the volume-element $d\tau$. We can obtain a similar formula for the current, or number of electrons crossing a given area per unit time. More exactly, we require a vector $\mathbf{j}$, at all points of space, such that $(\mathbf{j}\cdot d\mathbf{S}) \, dt$ is the probability that an electron will cross an element $d\mathbf{S}$ of area in the time dt. The required formula for $\mathbf{j}$ is

$$\mathbf{j} = \frac{h}{4\pi i m}\{\psi^*\,\mathrm{grad}\,\psi - \psi\,\mathrm{grad}\,\psi^*\}. \tag{18}$$

We shall show that this formula gives $\mathbf{j}$ correctly in all cases in which $\mathbf{j}$ could be measured.

In a region in which V is constant or zero, and in which there is a single stream of electrons moving in the direction $\mathbf{n}$, the wave function will be of the form

$$\psi = a \exp\{2\pi i m v \mathbf{n}\cdot\mathbf{r}/h\}$$

and $\mathbf{j}$ equal to $v|a|^2\mathbf{n}$, which is clearly given by (18).

To measure $\mathbf{j}$ in general, one would place a collector in the path of the electrons, and measure the charge falling on it per unit time. Such a procedure measures the average value of $\mathbf{j}$ over a region large compared with the wave-length, and this is the only thing that can be determined by direct experiment. If we suppose that V and therefore λ are constant in this region, then the wave function must be of the form

$$\psi = \sum_s a_s \exp\{2\pi i m v \mathbf{n}_s\cdot\mathbf{r}/h\},$$

where the $\mathbf{n}_s$ are unit vectors, and the a_s constants. This wave function represents streams of electrons superimposed on one another. The fact that according to the wave mechanics such streams should interfere will not affect the number of electrons falling on the collector, because the collector is large compared to the wave-length. If the area of the collector is A, and if it is normal to the direction $\mathbf{n}$, the number of electrons falling on it per unit time is

$$A \sum_s |a_s|^2 \mathbf{n}\cdot\mathbf{n}_s. \tag{19}$$

According to the formula (18) this number should be

$$\int \mathbf{j}\cdot\mathbf{n} \, dS$$

over the surface of A. This is easily seen to lead to the formula (19), since the cross terms of the type

$$a_s a_t^* \exp\{2\pi i m v (\mathbf{n}_s - \mathbf{n}_t)\cdot\mathbf{r}/h\}$$

become zero when averaged over an area large compared with the wave-length.

If the beams come from different sources, a_s must be taken to have the form $\alpha_s \exp(i\phi_s)$, where ϕ_s is an arbitrary phase having no relation to the corresponding phase ϕ_t. To obtain the current one must average (18) for all ϕ_s, ϕ_t; the cross terms will then vanish.

We shall refer to the vector **j** as the current vector, though it is only the averaged value of **j** that can be observed directly.

It may easily be shown from the wave equation that charge is conserved—i.e. that the average number of electrons moving into a volume is, in a steady beam, equal to the number moving out.† This will be so if div **j** vanishes. Now from (18) we have

$$\operatorname{div} \mathbf{j} = \frac{h}{4\pi i m}\{\psi^*\nabla^2\psi - \psi\nabla^2\psi^*\}.$$

But since both ψ and ψ^* satisfy Schrödinger's equation, it follows that

$$\psi^*\nabla^2\psi = -\psi^*\frac{8\pi^2 m}{h^2}(W-V)\psi$$

and that $\psi\nabla^2\psi^*$ is equal to the same expression. Thus we see that div **j** is zero.

8. Problems in which $|\psi|^2$ varies with the Time

Let us consider a highly evacuated discharge tube, in which a beam of electrons is projected against a screen in which there is an aperture covered by a shutter. Suppose that the aperture is suddenly opened; then, a short time t afterwards, there would be a stream of electrons coming out of the aperture, and extending a distance vt from the hole. v is what we call the 'velocity' of the electrons, and is connected with the energy W due to the field that has accelerated them by the formula

$$W = \tfrac{1}{2}mv^2.$$

From the point of view of the classical mechanics, this is trivial; however, according to our fundamental assumption, we ought to be able to predict this result by postulating the presence of a wave and then making the assumption that $|\psi|^2$ is equal to the number of electrons per unit volume. Now, from the wave point of view, we have a steady wave train falling on the screen, until the shutter is opened, when a beam passes out into space; the velocity with which the front of the beam advances is the *group velocity* of the waves.

† Compare Sommerfeld, *Wave Mechanics*, p. 89.

Now the group velocity in any wave-motion is equal to $d\nu/dN$, where ν is the frequency, and N the wave number, equal to the reciprocal of the wave-length λ. In order that the wave description may be in agreement with experiment (that is, in this case, with the classical theory), this velocity must be equal to the classical velocity of the electrons, namely, v. Thus we must have

$$\frac{d\nu}{dN} = v.$$

Expressing v in terms of N, we have

$$\frac{d\nu}{dN} = hN/m.$$

We may integrate this equation; we obtain

$$\nu = \tfrac{1}{2}hN^2/m + \text{const.}$$
$$= W/h + \text{const.}$$

The formula $\qquad\qquad h\nu = E,$

where E is the relativistic expression for the energy of a particle (including the rest-mass), namely,

$$E = mc^2(1 - v^2/c^2)^{-\frac{1}{2}},$$

was deduced by de Broglie[†] from considerations depending on the principle of relativity. If v/c is small compared with unity, this reduces to

$$h\nu = mc^2 + \tfrac{1}{2}mv^2,$$

which gives a value to the constant. However, the value of this constant does not affect any experimental result, and it is convenient to put it equal to zero in non-relativistic problems.

The wave equation for a general, non-monochromatic wave-disturbance is

$$\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2\psi - V\psi. \qquad (20)$$

This equation may most easily be obtained as follows: the equation satisfied by the wave function describing a stream of electrons of energy W is

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(W - V)\psi = 0. \qquad (21)$$

This wave function will be of the form

$$\psi = f(x, y, z)\exp(-2\pi i Wt/h), \qquad (22)$$

† de Broglie, *Ann. de Physique*, **10** (1925), 22.

as we have just shown. Now the equation which we require must not contain W; from (22) we see that

$$W\psi = -\frac{h}{2\pi i}\cdot\frac{\partial\psi}{\partial t},$$

and hence, from (21), it follows that equation (20) is satisfied by wave functions describing electrons all with the same energy—i.e. by wave functions of the type (22). But the most general wave function must be made up by superimposing such wave functions; therefore the most general wave function will satisfy (20).

From the wave equation (20) it may easily be shown that charge is conserved. If we denote by ρ the quantity $\psi\psi^*$, then $\int\rho\,d\tau$ integrated over any volume will be equal to the probability that an electron is in the volume. $\int\mathbf{j}\cdot d\mathbf{S}$ will be equal to the probability per unit time that an electron moves out of the volume. We must therefore have

$$\frac{\partial}{\partial t}\int\rho\,d\tau + \int\mathbf{j}\cdot d\mathbf{S} = 0. \tag{23}$$

This will be the case if $\qquad \dfrac{\partial\rho}{\partial t} + \operatorname{div}\mathbf{j} = 0. \tag{24}$

(24) may easily be proved from the wave equation (20), using the definition (18) of $\mathbf{j}$. For proof, cf. Sommerfeld, *Wave Mechanics*, p. 89.

9. Wave Packets

Let us suppose that a beam of electrons is fired at a screen in which there is an aperture, which is initially closed by some kind of shutter, and is then opened for a short time, and then closed again. If this experiment were carried out, a cloud of electrons would pass through the aperture and travel out into space. One could say that a region, in which the electron density is different from zero, would be travelling through space. The shorter the time during which the shutter is open, the smaller will this region be.

To describe this phenomenon in the language of wave mechanics, we must picture a train of de Broglie waves falling on the screen, and, when the shutter is opened, a 'wave packet' or 'wave group' passing through. The square of the amplitude of the wave function gives us, as usual, the probable electron density. The wave group as a whole will travel forward with the group velocity of the de Broglie waves, and this, as we have seen, is equal to the classical velocity of the electrons that they represent. The wave mechanics, therefore, makes the same predictions as the classical mechanics.

If $\psi(x, y, z, t)$ is the wave function at any point in the wave packet, then the number n, defined† by the integral (over all space)

$$n = \iiint |\psi(x, y, z, t)|^2 \, dx \, dy \, dz,$$

is equal to the probable number of electrons that have passed through the shutter. If the original electron beam were sufficiently weak, or if the shutter were only open for a very short time, then this number might be of order of magnitude unity. It must be remembered, of course, that if n were actually equal to unity, it would not mean that just one electron would pass through every time. It would mean, that if the experiment were repeated a very large number p times, the total number of electrons passing through would be pn, even though in individual experiments the number would be zero, one, two, and so on.

In discussing the behaviour of wave packets, it is usual to normalize the wave function in such a way that n is equal to unity.

The study of wave packets is of little use in enabling one to predict the results of real experiments; in practically all experiments with free electrons a continuous stream is used. Wave packets are, however, instructive in enabling one to understand the ideas of the wave mechanics, because they have a certain rather superficial resemblance to the *particles* of the classical theory. For instance, if one can show that a wave packet will follow the path of the classical particle, one may deduce that wave mechanics and classical mechanics will give the same result in a given problem.

9.1. *One-dimensional Motion of a Wave Packet in a Homogeneous Medium.*

In any kind of wave-motion there is a relation between the frequency ν and the wave number N. For de Broglie waves, in the non-relativistic theory, this relation is

$$\nu = \tfrac{1}{2} h N^2 / m.$$

We shall assume in this paragraph a quite general relationship,

$$\nu = \nu(N).$$

The most general possible wave disturbance is given by

$$\psi = \int\limits_{-\infty}^{+\infty} a(N) \, dN \, \exp[2\pi i(Nz - \nu t)],$$

where $a(N)$ is an arbitrary complex function. This wave disturbance

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† N is a constant with respect to the time; cf. § 8.

is obtained by superimposing an infinite number of plane waves, with arbitrary amplitudes and phases. We can choose $a(N)$ so that ψ has any desired form at time $t = 0$, by means of Fourier's integral theorem. We shall take for our wave packet at time $t = 0$

$$\psi = C \exp(2\pi i N_0 z - z^2/\sigma^2). \qquad (25)$$

The error function form for the amplitude is chosen because all the subsequent integrations can then be carried out in terms of known functions. The wave packet is thus initially in the neighbourhood of the origin, has wave-number N_0, and breadth of order of magnitude 2σ. It is easily seen (and will be proved below) that

$$a(N) = C\pi^{\frac{1}{2}}\sigma \exp[-(N-N_0)^2\pi^2\sigma^2]. \qquad (26)$$

To find the form of the wave packet at any subsequent time, we have therefore to evaluate the integral

$$\psi = \int\limits_{-\infty}^{\infty} C\pi^{\frac{1}{2}}\sigma \exp[2\pi i(Nz-\nu t)-(N-N_0)^2\pi^2\sigma^2] \, dN. \qquad (27)$$

To do this we expand ν in a Taylor's series

$$\nu = \nu_0 + (N-N_0)\nu_0' + \tfrac{1}{2}(N-N_0)^2\nu_0'' + ...,$$

where ν_0, ν_0', etc., denote the values of ν and its differential coefficients with respect to N, for the value $N = N_0$. Now if $\sigma \gg \lambda$, as we may assume to be the case, it is clear that most of the integral (27) comes from $N \sim N_0$; we shall therefore secure a good approximation if we neglect terms in $(N-N_0)^3$ in the expansion of ν. We may note that for de Broglie waves in the non-relativistic theory this approximation is exact, since ν is a quadratic function of N.

Writing $\qquad\qquad\qquad N-N_0 = \zeta,$

the equation (27) becomes

$$\psi = C\pi^{\frac{1}{2}}\sigma \int\limits_{-\infty}^{+\infty} \exp[-a\zeta^2+2b\zeta+c] \, d\zeta,$$

where

$$a = \pi^2\sigma^2 + \pi i\nu_0'' t,$$
$$b = -\pi i(\nu_0' t - z),$$
$$c = 2\pi i(N_0 z - \nu_0 t).$$

The integrand may be written

$$\exp\left[-a\left(\zeta-\frac{b}{a}\right)^2 + c + \frac{b^2}{a}\right].$$

Putting $\zeta - b/a = \eta$, we obtain for ψ

$$\psi = C\pi^{\frac{1}{2}}\sigma \exp\left(c + \frac{b^2}{a}\right) \int\limits_{-\infty}^{\infty} e^{-a\eta^2}\, d\eta$$

$$= C\pi\sigma a^{-\frac{1}{2}}\exp\left(c + \frac{b^2}{a}\right).$$

Putting in the values of a, b, c, we obtain

$$\psi = C\left[1 + \frac{iv_0''t}{\pi\sigma^2}\right]^{-\frac{1}{2}}\exp\left[2\pi i(N_0 z - \nu_0 t) - \frac{(\nu_0' t - z)^2}{\sigma^2 + iv_0'' t/\pi}\right].$$

The wave packet reduces to (25) at time $t = 0$, as it should. At time t the centre of the wave packet is at the point

$$z = \nu_0' t.$$

Thus the velocity of the wave packet is equal to the group velocity $d\nu/dN$. A further important property of the wave packet is the spreading. Considering the exponential term in ψ only, we have for the amplitude $|\psi|$,

$$\exp\left[\frac{-\sigma^2(\nu_0' t - z)^2}{\sigma^4 + (\nu_0'' t/\pi)^2}\right].$$

For large t, therefore, the breadth of the wave packet is of order of magnitude

$$2\nu_0'' t/\pi\sigma.$$

The wave packet therefore spreads as it goes along, and the velocity with which its length increases is

$$\frac{d^2\nu}{dN^2}\frac{2}{\pi\sigma}.$$

If the waves are de Broglie waves,[†] we have in the non-relativistic theory

$$\frac{d\nu}{dN} = \frac{hN}{m} = v \quad \text{and} \quad \frac{d^2\nu}{dN^2} = \frac{h}{m}.$$

We have therefore for ψ

$$\psi = C\left[1 + \frac{iht}{\pi m\sigma^2}\right]^{-\frac{1}{2}}\exp\left[\frac{-(vt-z)^2}{\sigma^2 + iht/\pi m} - 2\pi i\left(\frac{mv^2 t}{2h} - \frac{mvz}{h}\right)\right].$$

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† Wave packets of de Broglie waves have been considered by various authors. Darwin (*Proc. Roy. Soc.* A, **117** (1927), 258) has given the wave function for a three-dimensional wave packet in free space [equation (5.6)], a wave packet describing an electron under a constant electric force [equation (6.2)], and under constant magnetic field [equation (7.10)]. Wave packets are discussed by Condon and Morse, *Quantum Mechanics*, p. 219; Frenkel, *Wellenmechanik*, p. 60.

One of the most important properties of wave packets is that, if a wave packet passes through any electric or magnetic field which does not vary appreciably in a distance comparable with the size of the wave packet, then it will follow the classical path. A proof is given in various text-books.†

† See, for example: Dirac, *Quantum Mechanics*, p. 120; Frenkel, *Wellenmechanik*, p. 64; Debye, *Phys. Zeitschrift,* **28** (1927), 170; Ehrenfest, *Z. für Phys.*, **45** (1927), 455; Ruark, *Phys. Rev.*, **32** (1928), 1133.

THE THEORY OF THE SCATTERING OF A BEAM OF PARTICLES BY A CENTRE OF FORCE

1. Calculation of Scattered Intensity

The problem of the collision between an electron and an atom is a 'many-body' problem, and as such will be considered in Chapter VIII; in this chapter we shall consider the scattering of a stream of charged particles by a small spherically symmetrical region in which their potential energy is different from zero; we shall call this region the 'atom', and the potential energy of a particle at distance r from the nucleus will be denoted by $V(r)$. In Chapter VIII it is shown that the elastic scattering by atoms can, to a certain approximation, be treated in this way, and methods are given for the calculation of $V(r)$.

In experiments on the scattering of a beam of particles, one measures the number of scattered particles falling per unit time on an area dS placed at a distance r from the scattering atoms. For purposes of calculation we suppose that there is only one scattering atom. The number of particles falling on dS will then be proportional to the area dS and inversely to the square of the distance r. That is to say, the number is proportional to the solid angle $d\omega$ subtended by dS at the centre of the atom. We shall refer to the particles which hit dS as 'scattered through an angle θ into the solid angle $d\omega$'.

The number of particles scattered into the solid angle $d\omega$ is also proportional to the current per unit area in the incident beam. Suppose that N particles cross unit area per unit time in the incident beam. Let the number of particles scattered per unit time through an angle θ into the solid angle $d\omega$ be

$$N I(\theta)\, d\omega.$$

Then $I(\theta)$ is the quantity that we wish to calculate. $I(\theta)\, d\omega$ has the dimensions of an area, and will be referred to as the 'effective cross-section for scattering into the solid angle $d\omega$'.

We shall refer, in what follows, to the charged particles as electrons, though the analysis is applicable equally to any type of particle.

Let (x, y, z) denote the Cartesian coordinates of the electron at any moment, and (r, θ, ϕ) its spherical polar coordinates, the z-axis being the axis from which θ is measured.[†] We shall suppose the atom to be situated at the origin, and the potential energy of an electron distant

† i.e. $r\cos\theta = z,$ $r\sin\theta\, e^{i\phi} = x + iy.$

r from the origin to be $V(r)$. In this section we shall assume that $V(r)$ tends to zero faster than $1/r$; the case of Coulomb scattering will be considered in Chapter III. We shall suppose that a stream of electrons moves with velocity v from left to right along the z-axis. We represent this stream of electrons by the plane wave $\exp(ikz)$, where k is equal to $2\pi mv/h$. This wave represents a density of electrons of one per unit volume, and therefore a flow of v electrons across unit area per unit time. The wave will be scattered by the atom, the amplitude of the scattered wave at the point (r, θ, ϕ) being, let us say,

$$r^{-1}f(\theta)e^{ikr}.$$

Our problem is to find the function $f(\theta)$. From it we can deduce the number scattered into a given solid angle per unit time. The number of electrons in the scattered wave crossing an element of area dS at the point (r, θ, ϕ) is $vr^{-2}\,dS|f(\theta)|^2$ per unit time; and therefore, if the incident beam is such that *one* electron falls on unit area per unit time, the number $I(\theta)\,d\omega$ scattered into a given solid angle $d\omega$ per unit time is equal to $|f(\theta)|^2\,d\omega$. We have therefore

$$I(\theta) = |f(\theta)|^2.$$

The number of particles scattered between angles θ and $\theta+d\theta$ is

$$|f(\theta)|^2\,2\pi\sin\theta\,d\theta.$$

Our problem, then, is to find a solution ψ of the wave equation which, at a large distance from the atom, represents an incident wave and a scattered wave. That is to say, we must have, for large r,

$$\psi \sim e^{ikz}+r^{-1}e^{ikr}f(\theta). \tag{1}$$

The wave equation satisfied by ψ (Schrödinger's equation) may be written

$$\nabla^2\psi+[k^2-U(r)]\psi = 0, \tag{2}$$

where $$k = 2\pi mv/h, \qquad U(r) = \frac{8\pi^2 m}{h^2}V(r).$$

Before considering the solution of (2) we require a certain expansion in spherical harmonics (eq. (8)), which will now be proved.

The plane wave e^{ikz} is a solution of the equation

$$\nabla^2\psi+k^2\psi = 0. \tag{3}$$

The equation can also be solved in spherical polar coordinates; it is easily seen that

$$\psi = P_n(\cos\theta)f_n(r)$$

is a solution, if f_n is a solution of the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right)+\left(k^2-\frac{n(n+1)}{r^2}\right)f = 0 \tag{4}$$

and $P_n(\cos\theta)$ is the nth Legendre coefficient.† The equation (4) can be solved in series; there are two solutions, one beginning with r^n and the other with r^{-n-1}; they are expressible in terms of Bessel functions (cf. eq. (9)). Let us denote by $f_n(r)$ the solution of (4) that is bounded at $r = 0$. Then, except for an arbitrary multiplying constant, $f_n(r)$ is determined.

Clearly, if the A_n are arbitrary constants,

$$\sum_{n=0}^{\infty} A_n P_n(\cos\theta)f_n(r) \tag{5}$$

is a solution of (3), and we know further that this is the most general solution of (3) which has axial symmetry (i.e. does not involve ϕ), and which is finite at the origin. It follows that e^{ikz} can be expanded in this form.

Let, then,

$$e^{ikz} = e^{ikr\cos\theta} = \sum_{n=0}^{\infty} A_n P_n(\cos\theta)f_n(r).$$

To obtain A_n we multiply both sides by $P_n(\cos\theta)\sin\theta$ and integrate from 0 to π. Putting $\cos\theta = t$, we obtain

$$\frac{2}{2n+1}A_n f_n(r) = \int_{-1}^{+1} e^{ikrt}P_n(t)\,dt. \tag{6}$$

f_n has been defined except for an arbitrary multiplying constant, and A_n cannot be determined until this is given. We can define f_n exactly by means of its asymptotic expansion for large r; integrating the right-hand side of (6) by parts, we obtain

$$\frac{1}{ikr}[e^{ikrt}P_n(t)]_{t=-1}^{t=+1} - \frac{1}{ikr}\int e^{ikrt}P_n'(t)\,dt.$$

The second term is of order $1/r^2$; for large r, therefore, we have

$$\frac{2}{2n+1}A_n f_n(r) \sim \frac{1}{ikr}[e^{ikrt}P_n(t)]_{-1}^{+1}.$$

Since $P_n(1) = 1$, $P_n(-1) = (-1)^n$, the right-hand side of this equation is equal to

$$2i^n(kr)^{-1}\sin(kr-\tfrac{1}{2}n\pi).$$

If now we determine f_n completely by stipulating that it shall be that

† Whittaker and Watson, *Modern Analysis*, p. 302.

solution of (4) which has the asymptotic form

$$f_n(r) \sim (kr)^{-1}\sin(kr - \tfrac{1}{2}n\pi), \tag{7}$$

then we see that A_n is equal to $(2n+1)i^n$, and therefore

$$e^{ikz} = \sum_{n=0}^{\infty} (2n+1)i^n P_n(\cos\theta)f_n(r), \tag{8}$$

which is the required expansion. For reference we give here the expressions for f_n in terms of Bessel functions, viz.

$$f_0(r) = \sin kr/kr$$
$$f_n(r) = (\pi/2kr)^{\frac{1}{2}}J_{n+\frac{1}{2}}(kr). \tag{9}$$

Let us now consider the wave equation (2) for an electron in the field of an atom. As before, the general solution of (2) having axial symmetry is

$$\psi = \sum_{n=0}^{\infty} A_n P_n(\cos\theta)L_n(r), \tag{10}$$

where the A_n are arbitrary constants, and L_n is any solution of

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2}\right)L = 0. \tag{11}$$

As before, (11) has two independent solutions,† one finite at the origin and the other infinite. We wish to choose the constants A_n so that (10) shall represent an incident wave and a scattered wave—i.e. so that (10) shall have the asymptotic form (1). It is necessary that our wave function should be everywhere finite; L_n must therefore be chosen to be that solution of (11) that is finite at the origin. $L_n(r)$ is then defined except for an arbitrary multiplying constant.

If we set $\qquad\qquad L_n(r) = r^{-1}G(r),$

equation (11) reduces to

$$\frac{d^2G}{dr^2} + \left[k^2 - U(r) - \frac{n(n+1)}{r^2}\right]G = 0. \tag{12}$$

For large r the last two terms in the bracket tend to zero, and we should therefore expect that the asymptotic form of *any* solution G would be

$$G \sim A\sin(kr + \epsilon), \tag{13}$$

where A and ϵ are constants.

To test whether this is so, we set

$$G = u(r)e^{ikr}.$$

† We assume that if $U(r)$ has a pole at the origin, it is not of higher order than r^{-1}. Cf. § 3.

Substituting in (12), we obtain

$$\frac{d^2u}{dr^2} + 2ik\frac{du}{dr} - \left[U + \frac{n(n+1)}{r^2} \right]u = 0. \tag{14}$$

For large r, we may assume, since u is nearly a constant,

$$\frac{d^2u}{dr^2} \ll k\frac{du}{dr}.$$

Neglecting the former term, we can integrate (14); we obtain

$$2ik\log u = \int^r \left[U(r) + \frac{n(n+1)}{r^2} \right] dr.$$

The right-hand side tends to a constant for large r if, and only if, $U(r)$ tends to zero faster than $1/r$ as r tends to infinity. Thus for fields which fall to zero faster than the Coulomb field, G has the asymptotic form (13). The case of the Coulomb field is considered in Chapter III.

The particular solution of (11) that is finite at the origin will therefore have the form

$$Cr^{-1}\sin(kr - \tfrac{1}{2}n\pi + \eta_n),$$

where C is an *arbitrary* constant, and† η_n is a constant that depends on k and on $U(r)$, and which can in general only be determined by numerical integration (cf. § 3). To fix the arbitrary constant C, we define $L_n(r)$ to be that bounded solution of (11) that has the asymptotic form

$$(kr)^{-1}\sin(kr - \tfrac{1}{2}n\pi + \eta_n). \tag{15}$$

We have to choose the constants A_n in (10). If we subtract the expression (8) for the incident plane wave, we obtain the expression for the scattered wave. We have to choose the A_n so that this does actually represent a scattered wave—i.e. so that there are no terms of the type $r^{-1}e^{-ikr}$ in the asymptotic expansion. Thus for all n we must have, for large r,

$$A_n L_n(r) - (2n+1)i^n f_n(r) \sim C_n r^{-1}e^{ikr},$$

where C_n is some constant. Putting in the asymptotic expressions for L_n, f_n, we obtain for the left-hand side

$$\frac{e^{ik\rho}}{2ikr}[A_n e^{i\eta_n} - (2n+1)i^n] - \frac{e^{-ik\rho}}{2ikr}[A_n e^{-i\eta_n} - (2n+1)i^n],$$

where

$$k\rho = kr - \tfrac{1}{2}n\pi.$$

Choosing A_n so that the second term shall vanish, we have

$$A_n = (2n+1)i^n e^{i\eta_n}.$$

For the wave function, therefore, that represents the incident wave and

† The term $-\tfrac{1}{2}n\pi$ is added so that if $U(r)$ is zero η_n shall be zero.

the scattered wave, we have

$$\psi = \sum_{n=0}^{\infty} (2n+1)i^n e^{i\eta_n} L_n(r) P_n(\cos\theta), \tag{16}$$

and for the asymptotic form of the scattered wave

$$r^{-1}e^{ikr}f(\theta),$$

with

$$f(\theta) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1)[e^{2i\eta_n}-1]P_n(\cos\theta). \tag{17}$$

This gives us our expression for the amplitude of the scattered wave. It will be noticed that $f(\theta)$ is complex; the scattered intensity $I(\theta)$ is given by the square of the modulus, i.e. by A^2+B^2, where

$$A = \frac{1}{2k} \sum (2n+1)[\cos 2\eta_n - 1]P_n,$$

$$B = \frac{1}{2k} \sum (2n+1)\sin 2\eta_n P_n.$$

These series are, in general, convergent (cf. § 2). There is only one case in which the series (17) can be summed in terms of known functions, namely, the scattering by a Coulomb field, which we shall consider in Chapter III. We shall find there that the scattered intensity is the same as that given by the classical theory. This is not true of any other field that has been investigated.

The *total elastic cross-section* Q of an atom for electrons of a given velocity is defined as the total number of electrons scattered elastically by the atom, per unit time, from a beam of unit intensity, i.e. such that one electron crosses unit area per unit time. In practice the number scattered through an angle greater than some small angle θ_0 is measured, but since $f(\theta)$ is bounded at $\theta = 0$ for atomic fields, Q is very insensitive to θ_0, and thus θ_0 may be taken to be zero.[†]

The formula for Q is

$$Q = 2\pi \int_0^{\pi} |f(\theta)|^2 \sin\theta \, d\theta.$$

This gives

$$Q = \frac{4\pi}{k^2} \sum_{n=0}^{\infty} (2n+1)\sin^2\eta_n. \tag{18}$$

The method of this section was first used by Rayleigh.[‡] It was first applied to the problem of the scattering of electrons by atoms by Faxén and Holtsmark.[§]

[†] Cf. Ch. X, § 1.   [‡] *Theory of Sound,* ii. 323.
[§] *Zeits. f. Physik,* **45** (1927), 307.

2. Connexion between the Phases η_n and the Angular Momentum of the Scattered Particle

The phases η_n that occur in the expression (17) for the scattered amplitude are, as we have seen, defined in the following way. Let $G_n(r)$ be the bounded solution of

$$G'' + \left[k^2 - U(r) - \frac{n(n+1)}{r^2} \right] G = 0, \tag{19}$$

where the dashes denote differentiation with respect to r. Then, for large r, G will have the asymptotic form

$$G \sim \sin(kr - \tfrac{1}{2}n\pi + \eta_n);$$

η_n is thus defined.

If $U(r)$ falls exponentially to zero for large r, it is possible to make an estimate of the value of η_n for fairly large n, and thus to estimate the number of terms required to sum the series (17) for $f(\theta)$. The convergence of the series may also be tested in this way.

Let us denote by $F(r)$ the function

$$F(r) = k^2 - U(r) - \frac{n(n+1)}{r^2}. \tag{20}$$

If $U(r)$ has no pole of higher order than r^{-1}, $F(r)$ is negative for small r and positive for large r, and has therefore at least one zero. For simplicity we shall suppose that $F(r)$ has only one zero, which we call r_n.

The solution G of equation (19) behaves for small r like Ar^{n+1}, where A is a constant which we shall assume positive. Thus for small r, both G and G' are positive, and we see from (19) that G'' is positive also. Now, for increasing r, G cannot decrease until G' changes sign, and this can only happen for a value of r greater than the first zero of G''. But since G is increasing and therefore positive until the first zero of G'', it follows from (19) that this zero is at the point r_n. Thus G increases (exponentially) until the point $r = r_n$. The proof is similar if A is negative.

For $r > r_n$, G is an oscillating function, as shown in Fig. 2.

Let us now find the closest distance of approach, according to the classical theory, of an electron of energy E fired at an atom, in such a way that its angular momentum about the nucleus is I. I is the product of the initial momentum of the electron and the 'impact parameter'† p. If v be the velocity of the electron at the point of closest

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† The 'impact parameter' is the distance between the initial line of motion of the particle and the centre of the scattering field.

approach, we have, firstly, since energy is conserved,

$$\tfrac{1}{2}mv^2 + V(r) = E,$$

and secondly, by the principle of conservation of angular momentum, since the radial velocity is zero at the point of closest approach,

$$mvr = I.$$

Eliminating v, we obtain for r the equation

$$E - V(r) - I^2/2mr^2 = 0. \tag{21}$$
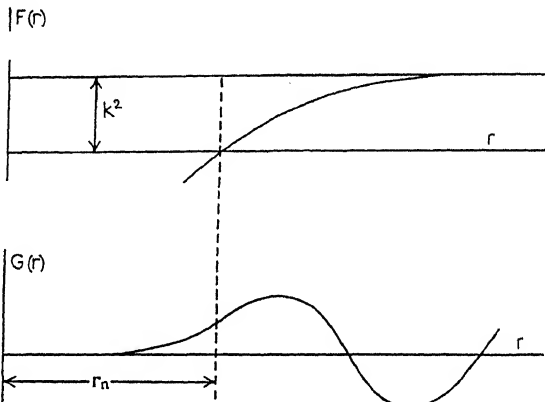
FIG. 2

If we put

$$I = h[n(n+1)]^{\frac{1}{2}}/2\pi, \tag{22}$$

then equation (21) is equivalent to

$$F(r) = 0,$$

$F(r)$ being defined by (20). Thus the zero r_n of $F(r)$ is the distance to which a particle of angular momentum given by (22) would approach, according to the classical theory.

We have already seen that $|G_n(r)|$ is very small for r much less than r_n. We shall now show that if n is so big that a particle with angular momentum I given by (22) does not penetrate the atom (according to the classical theory), then the corresponding phase η_n is very small. We have to show, therefore, that if $V(r_n)$ is very small for n greater than a certain value, η_n is also very small for these values of n. We note that if $V(r_n)$ is very small, r_n is approximately the zero of

$$k^2 - n(n+1)/r^2.$$

Let now $g_n(r)$ be that solution of the equation

$$\frac{d^2g}{dr^2} + \left(k^2 - \frac{n(n+1)}{r^2}\right)g = 0 \tag{23}$$

which is bounded at the origin, the arbitrary multiplying constant being chosen in such a way that

$$g_n \sim \sin(kr - \tfrac{1}{2}n\pi)$$

for large r. g_n is equal to†

$$(\pi kr/2)^{\frac{1}{2}} J_{n+\frac{1}{2}}(kr).$$

It follows from the arguments given above that g_n decreases exponentially as r decreases, for r less than r_n. The form of the function is similar to that of the function G illustrated in Fig. 2.

We now solve the wave equation (19) by a perturbation method. We put

$$G_n = g_n + \Phi$$

and assume that the product ΦU can be neglected. Substituting into the equation (19), we obtain for Φ,

$$\frac{d^2\Phi}{dr^2} + \left[k^2 - \frac{n(n+1)}{r^2} \right]\Phi = U(r)g_n(r). \tag{24}$$

Let

$$\Phi = g_n(r)\zeta(r).$$

Then, substituting in (24), we obtain

$$\zeta'' g_n + 2\zeta' g_n' = U(r)g_n(r).$$

Multiplying this equation by $g(r)$, and integrating, we obtain

$$\zeta' g^2 = \int^r U(r)[g(r)]^2 \, dr.$$

Since ζ' must be bounded at $r = 0$, and $g(r)$ behaves like r^{n+1} for small r, the lower limit of integration must be zero. Thus we see that

$$\frac{d\zeta}{dr} = [g(r)]^{-2} \int_0^r U(r)[g(r)]^2 \, dr.$$

For large r we have therefore

$$\frac{d\zeta}{dr} \sim \mathrm{cosec}^2(kr - \tfrac{1}{2}n\pi) \int_0^\infty U(r)[g(r)]^2 \, dr, \tag{25}$$

since the integral on the right converges.

Let us denote by A_n the integral

$$\int_0^\infty U(r)[g_n(r)]^2 \, dr.$$

We have postulated that, for the value of n considered, $U(r)$ is small for $r > r_n$, and we know that g_n is small for $r < r_n$. Thus A_n is small.

† Cf. equation (9).

Integrating (25), we obtain

$$\zeta \sim -[\cot(kr-\tfrac{1}{2}n\pi)+\alpha]A_n/k,$$

where α is a constant. Hence we obtain

$$G_n \sim \sin(kr-\tfrac{1}{2}n\pi)-[\cos(kr-\tfrac{1}{2}n\pi)+\alpha\sin(kr-\tfrac{1}{2}n\pi)]A_n/k.$$

Neglecting terms involving the square of η_n, we see that

$$G_n \sim \text{const.} \sin(kr-\tfrac{1}{2}n\pi+\eta_n), \tag{26}$$

where $\qquad\qquad\qquad \eta_n = -A_n/k.$

Writing out this formula for η_n in full, we obtain

$$\eta_n = -\tfrac{1}{2}\pi\frac{8\pi^2 m}{h^2}\int_0^\infty V(r)[J_{n+\frac{1}{2}}(kr)]^2 r\, dr. \tag{27}$$

The formula is valid if the right-hand side is small, and shows that η_n is small under the conditions stated.

The formula (27), being valid for large n, may be used to test the convergency of series (17) for the scattered amplitude. The series converges if

$$\sum \eta_n P_n(\cos\theta)(2n+1)$$

converges.

If $\eta_n \ll 1$ for all n, the formula (27) may be used for all n. We then obtain for the scattered amplitude

$$f(\theta) = \frac{1}{k}\sum_{n=0}^\infty (2n+1)\eta_n P_n(\cos\theta). \tag{28}$$

The series may be summed and yields the well-known Born formula (cf. Chap. VII, § 2).

3. Examples on the Theory of Scattering by a Central Field

Examples of the application of this theory to the scattering of electrons by atoms are given in Chapter X of this book; we give here certain very simple examples which may help to illustrate the theory.

3.1. *Scattering by a 'Potential Hole'.*

We take for the potential of the electron in the field of the 'atom'

$$V(r) = -D \qquad (r < a)$$
$$= 0 \qquad (r > a).$$

We shall suppose that the wave-length λ is very much greater than a, so that all the phases η_n are negligible except the first, η_0. [Note that the distance of closest approach of a particle with one quantum of angular momentum is $\lambda/2\pi$, if the particle does not enter the potential

hole.] The wave scattered by the atom is then

$$\frac{e^{ikr}}{r} \frac{1}{2ik}[e^{2i\eta_0} - 1].\tag{29}$$

To find η_0 we have to find the asymptotic form of the solution of

$$\frac{d^2G}{dr^2} + \frac{8\pi^2 m}{h^2}(E - V)G = 0$$

which vanishes at the origin [since $r^{-1}G$ must be bounded]. The solution is

$$A \sin k'r \qquad (k'^2 = 8\pi^2 m(E + D)/h^2, \; r < a)$$
$$\sin(kr + \eta_0) \qquad (k^2 = 8\pi^2 mE/h^2, \; r > a).$$
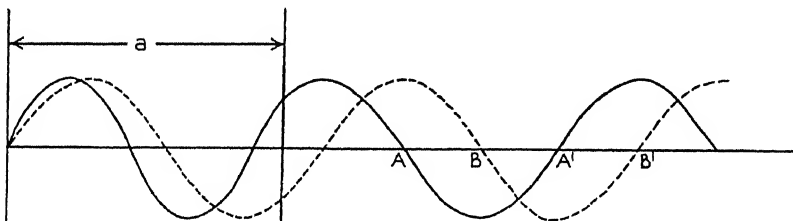
FIG. 3

The constants A and η_0 must be chosen in such a way that G and dG/dr are continuous at $r = a$; i.e. in such a way that

$$A \sin k'a = \sin(ka + \eta_0)$$
$$Ak' \cos k'a = k \cos(ka + \eta_0).$$

These two equations give us for η_0

$$\eta_0 = \tan^{-1}\left(\frac{k}{k'} \tan k'a\right) - ka.\tag{30}$$

In Fig. 3 the wave function G is shown by the full line; the dotted line represents the curve $\quad G = \sin kr.$

The phase η_0 is represented by the length AB, or $A'B'$, multiplied by k. It will be seen from the figure that η_0 is positive for an attractive field; for a repulsive field it is easily seen that η_0 is negative.

As the velocity of the electrons tends to zero, η_0 in general tends to zero also, as may be seen from equation (30). The scattered intensity, given by the square of (29), tends therefore to a finite limit. If

$$\lim_{k \to 0} \frac{\tan k'a}{k'} = a,$$

then this limit is zero. If, on the other hand,

$$\lim_{k \to 0} \tan k'a = \infty,$$

then η_0 does not tend to zero, and the scattered intensity becomes infinite. It is possible therefore that the cross-section of an atom for very slow electrons may be either much larger or much smaller than the region in which $V(r)$ is comparable with the energy of the electron.

3.2. Scattering by a Small Impenetrable Sphere.

We assume as before that the radius a of the sphere is much less than $\lambda/2\pi$, so that only the first harmonic need be considered. Since the wave function must vanish at the surface of the sphere, we have

$$G = \sin k(r-a).$$

Thus

$$\eta_0 = -ak.$$

The effective cross-section is (eq. 18)

$$4\pi k^{-2} \sin^2 \eta_0,$$

which, since $\eta_0 \ll 1$, may be replaced by $4\pi a^2$. Thus the cross-section calculated by means of wave mechanics is four times that calculated from the classical theory.

3.3. Scattering by an Inverse Cube Law Field.

Let the potential energy at distance r from the nucleus be γr^{-2}. Then the wave equation to determine L is

$$\frac{d^2L}{dr^2} + \frac{2}{r}\frac{dL}{dr} + \left(k^2 - \frac{n(n+1)+\beta}{r^2}\right)L = 0 \qquad (\beta = 8\pi^2 m\gamma/h^2). \qquad (31)$$

The solutions of this equation are

$$r^{-\frac{1}{2}}J_{\nu+\frac{1}{2}}(kr), \qquad (32)$$

where ν is either root of

$$\nu(\nu+1) = n(n+1)+\beta, \qquad (33)$$

i.e.

$$\nu = \tfrac{1}{2}[-1 \pm (1+4n+4n^2+4\beta)^{\frac{1}{2}}].$$

Now our wave function $L(r)$ must be finite at the origin. That is to say, since $r^{-\frac{1}{2}}J_{\nu+\frac{1}{2}}$ behaves like r^ν at the origin, we must have

$$\nu \geqslant 0 \qquad \text{(all } n\text{)}.$$

If β is positive (repulsive field), then this condition is satisfied for one root and not the other. Thus the bounded solution is unique, as it is for fields with a lower singularity. If β is negative (attractive field), there are then two possibilities; if $-\tfrac{1}{4} < \beta < 0$, then for $n = 0$ both solutions are unbounded at the origin, but there is one solution for which the singularity is of a lower order than for any other solution,

and if we choose to take this as our solution, then a formula for the scattered intensity may be obtained. If, on the other hand, $\beta < -\frac{1}{4}$, *both* solutions behave like $r^{-\frac{1}{2}}\exp(\pm i\alpha \log r)$ near the origin. *There is therefore no solution of the scattering problem.* It is not merely that a singularity of this type at the origin is objectionable. There is no solution because there is no criterion as to which solution of equation (31) ought to be taken, and thus the phase η_0 cannot be defined.

Returning to the case of the repulsive field, we see from the asymptotic form of (32) that

$$\eta_n = \tfrac{1}{2}\pi(\nu - n),$$

where ν is the positive root of equation (33). For large n this reduces to

$$\tfrac{1}{2}\pi\beta/(2n+1).$$

The reader will easily verify that formula (27) gives the same result.

SCATTERING OF A BEAM OF PARTICLES BY A COULOMB FIELD

1. Introduction

If a beam of charged particles, each carrying a charge $Z'\epsilon$, and such that one particle crosses unit area per unit time, falls on a single nucleus of infinite mass and charge $Z\epsilon$, then, according to Newtonian mechanics, the number of particles $I(\theta)\,d\omega$ scattered per unit time through an angle θ into the solid angle $d\omega$ is given by

$$I(\theta) = (ZZ'\epsilon^2/2mv^2)^2 \operatorname{cosec}^4 \tfrac{1}{2}\theta, \qquad (1)$$

where m, v are the mass and velocity of the incident particles. This formula was first deduced by Rutherford; the proof is given in various text-books, and will not be reproduced here.† It is in agreement with experiment for the scattering of α-particles by heavy nuclei.

In this chapter we shall show that exactly the same formula may be deduced from the wave mechanics. We have therefore to consider the scattering of a stream of charged particles (electrons or α-particles) by a bare nucleus, the force between a particle and the nucleus varying as the inverse square of the distance. For $V(r)$, therefore, we have

$$V(r) = -Z\epsilon^2/r \qquad \text{(electrons)},$$

and $\qquad V(r) = 2Z\epsilon^2/r \qquad (\alpha\text{-particles}),$

where Z is the atomic number of the scattering nucleus.

We shall write in general

$$V(r) = ZZ'\epsilon^2/r, \qquad (2)$$

where $Z'\epsilon$ is the charge on the scattered particle, and Z' is to be taken positive or negative, according as the scattered particle is positively or negatively charged. The wave equation therefore is

$$\nabla^2\psi + \frac{8\pi^2 m}{\hbar^2}\left(E - \frac{ZZ'\epsilon^2}{r}\right)\psi = 0. \qquad (3)$$

We have to show that a solution can be obtained with the asymptotic form

$$\psi \sim I + S f(\theta), \qquad (4)$$

where I represents an incident wave, S the scattered wave, and

$$|f(\theta)| = (ZZ'\epsilon^2/2mv^2)\operatorname{cosec}^2 \tfrac{1}{2}\theta. \qquad (5)$$

We saw in Chapter II that the method given there for the calculation

† Cf. Rutherford, Chadwick, and Ellis, *Radiations from Radioactive Substances*, p. 191; or Andrade, *The Structure of the Atom*, p. 21.

of the scattered amplitude is only applicable if $V(r)$ tends to zero faster than r^{-1} as r tends to infinity. This limitation arises from the fact that the bounded solution $L_n(r)$ of the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right)+\left[\frac{8\pi^2 m}{h^2}\left(E-\frac{ZZ'\epsilon^2}{r}\right)-\frac{n(n+1)}{r^2}\right]L = 0 \qquad (6)$$

has asymptotic form†

$$(kr)^{-1}\sin(kr-\tfrac{1}{2}n\pi+\eta_n-\alpha\log 2kr) \qquad (\alpha = 2\pi ZZ'\epsilon^2/hv), \qquad (7)$$

which differs by the logarithmic term from the form assumed in Chap. II, eq. (15). Nevertheless, it has been shown by Gordon‡ that, corresponding to Chap. II, eq. (16), the wave function that describes the scattering is

$$\psi(r,\theta) = \sum_{n=0}^{\infty}(2n+1)i^n e^{i\eta_n}L_n(r)P_n(\cos\theta). \qquad (8)$$

This function is shown by Gordon to be equal to§

$$e^{-\frac{1}{2}\pi\alpha}\Gamma(1+i\alpha)e^{ikr\cos\theta}{}_1F_1(-i\alpha;1;ikr(1-\cos\theta)), \qquad (9)$$

and to have the asymptotic form

$$I+S\,f(\theta),$$

with

$$I = \exp[ikz+i\alpha\log k(r-z)], \qquad (10)$$

$$S = r^{-1}\exp[ikr-i\alpha\log kr], \qquad (11)$$

and $|f(\theta)|$ given by (5). For the phase of $f(\theta)$, cf. eq. (16) of this chapter.

The forms (10), (11) for the incident and scattered waves are peculiar to the Coulomb field. They may be explained as follows.

If we consider all the classical hyperbolic orbits with one asymptote pointing from right to left parallel to the z-axis, we should expect the wave front of the incident wave to be normal to all these hyperbolae. At large distances from the nuclei, the surface perpendicular to these hyperbolae does not tend to the form $z = $ constant, but, as has been shown by Gordon,‖ to the form

$$z+\frac{ZZ'\epsilon^2}{mv^2}\log k(r-z) = \text{const.}$$

The incident wave is, as it were, distorted even at infinity by the nucleus that it is going to encounter. Thus we should expect the

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† This is proved in § 4, where η_n is found.
‡ Gordon, *Zeits. f. Physik*, 48 (1928), 180.
§ The function ${}_1F_1$ is defined in § 3 of this chapter.
‖ Gordon, loc. cit.

incident wave to be

$$\exp\left\{ik\left[z+\frac{ZZ'\epsilon^2}{mv^2}\log k(r-z)\right]\right\},$$

which is the same as (10). The form of the scattered wave (11) may be explained in the same way.

In the following sections we shall show that (9) is a solution of the wave equation, and that it has the asymptotic form given by (10), (11), and (5). We shall not make use of the series (8) as in Gordon's method, but shall solve the wave equation directly. The method is one first given by Temple.†

2. Solution of the Wave Equation for Scattering by a Coulomb Field

The wave equation that we have to solve is

$$\nabla^2\psi+\left(k^2-\frac{\beta}{r}\right)\psi = 0 \qquad (\beta = 8\pi^2 mZZ'\epsilon^2/h^2). \tag{12}$$

We make the following substitution: we put

$$\psi = e^{ikz}F, \tag{13}$$

and obtain

$$\nabla^2F+2ik\frac{\partial F}{\partial z}-\frac{\beta F}{r} = 0.$$

This partial differential equation possesses a solution of the type

$$F = F(r-z);$$

if we make this substitution we obtain

$$2\left(1-\frac{z}{r}\right)F''+\frac{2}{r}F'+2ik\left(\frac{z}{r}-1\right)F'-\frac{\beta}{r}F = 0,$$

F', F'' being the first and second differential coefficients of F. If we multiply this equation by r we see that r, z only occur in the form $r-z$, and therefore a solution exists of the required type. Putting

$$\zeta = r-z,$$

we obtain

$$\zeta\frac{d^2F}{d\zeta^2}+\frac{dF}{d\zeta}-ik\zeta\frac{dF}{d\zeta}-\tfrac{1}{2}\beta F = 0. \tag{14}$$

If we try for a solution

$$F = \zeta^\rho(1+a_1\zeta+a_2\zeta^2+...),$$

the indicial equation gives $\rho^2 = 0$, and the solution finite at the origin is therefore of the form

$$F = \sum_{n=0}^{\infty}a_n\zeta^n.$$

† *Proc. Roy. Soc.* A, **121** (1928), 673.

Substituting this into (14), and equating to zero the coefficient of ζ^n, we obtain the recurrence formula

$$[n(n+1)+(n+1)]a_{n+1} = a_n[ikn+\tfrac{1}{2}\beta],$$

and therefore

$$a_{n+1} = (ik)^{n+1}\prod_{s=0}^{n}\frac{(s+\tfrac{1}{2}\beta/ik)}{(s+1)^2}.$$

It follows that F is a hypergeometric function of the kind described in § 3; we have

$$F = {}_1F_1(-i\alpha; 1; ik\zeta),$$

where

$$\alpha = \tfrac{1}{2}\beta/k = 2\pi ZZ'\epsilon^2/hv.$$

The asymptotic expansion of F will be found in § 3; we see, from equation (24), that $F = W_1 + W_2$, where for large r

$$W_1 \sim (-ik\zeta)^{i\alpha}G_1/\Gamma(1+i\alpha),$$
$$W_2 \sim (ik\zeta)^{-i\alpha-1}e^{ik\zeta}G_2/\Gamma(-i\alpha),$$

where

$$G_1 = 1+\frac{-\alpha^2}{ik\zeta}+\dots$$

$$G_2 = 1+(1+i\alpha)^2/ik\zeta+\dots.$$

Taking the expansions as far as terms in ζ^{-1}, we have therefore

$$W_1 \sim \frac{e^{\frac{1}{2}\pi\alpha}}{\Gamma(1+i\alpha)}\left(1-\frac{\alpha^2}{ik\zeta}\right)\exp(i\alpha\log k\zeta)$$

$$W_2 \sim \frac{-ie^{\frac{1}{2}\pi\alpha}}{\Gamma(-i\alpha)}\frac{e^{ik\zeta}}{k\zeta}\exp(-i\alpha\log k\zeta).$$

The functions W_1, W_2, when multiplied by $\exp(ikz)$, represent the incident and scattered waves respectively. Since we require an incident wave of unit amplitude, we take for the total wave function representing the scattering†

$$\psi(r,\theta) = e^{-\frac{1}{2}\pi\alpha}\Gamma(1+i\alpha)e^{ikz}{}_1F_1(-i\alpha; 1; ik\zeta), \tag{15}$$

where

$$\alpha = 2\pi ZZ'\epsilon^2/hv, \qquad \zeta = r-z = r(1-\cos\theta).$$

This wave function then has the asymptotic form

$$\psi \sim I+S f(\theta),$$

where

$$I = [1-\alpha^2/ik(r-z)]\exp[ikz+i\alpha\log k(r-z)],$$

$$S = r^{-1}\exp[ikr-i\alpha\log kr],$$

$$f(\theta) = \frac{ZZ'\epsilon^2}{2mv^2}\operatorname{cosec}^2\tfrac{1}{2}\theta\exp[-i\alpha\log(1-\cos\theta)+i\pi+2i\eta_0], \tag{16}$$

† Sommerfeld, *Ann. d. Physik*, **11** (1931), 257, has given the following formula for this function,

$$\psi(r,\theta) = e^{-\frac{1}{2}\pi\alpha}e^{ikr}\int_0^\infty x^{i\alpha}e^{-x}I_0(2\sqrt{ik\zeta x})\,dx,$$

where I_0 is the Bessel function defined in Whittaker and Watson, 4th edition, p. 372.

where
$$\exp 2i\eta_0 = \Gamma(1+i\alpha)/\Gamma(1-i\alpha).$$

It is to be noted that Z' in these formulae is to be taken as $+2$ for α-particles, -1 for electrons.

The incident wave fronts and the scattered wave fronts have the forms (10) and (11).

The scattered intensity $I(\theta)$ is given by

$$I(\theta) = |f(\theta)|^2 = \left[\frac{ZZ'\epsilon^2}{2mv^2}\right]^2 \operatorname{cosec}^4 \tfrac{1}{2}\theta,$$

which is the Rutherford formula.

NOTE

At the origin (15) gives $|\psi|^2 = 2\pi\alpha/(e^{2\pi\alpha}-1).$ (17)

For the case of a repulsive field, as between an α-particle and a nucleus, α is positive. If α is large and positive, e.g. for slow α-particles, $|\psi|^2$ is very small at the origin. This means that very few particles come near the nucleus.

If α is large and negative, e.g. for slow electrons, $|\psi|^2$ is fairly large at the origin, of order of magnitude $|\alpha|$.

If α is small, the solution (15) becomes at all points not very different from the plane wave $\exp(ikz)$.

That α should be small is also the condition of applicability of the Born approximation (Chap. VII), which consists in treating $V(r)$ as a perturbation. This may be seen by writing the wave equation in units of length $1/k$; we obtain

$$\nabla^2\psi + (1-2\alpha/r)\psi = 0.$$

3. The Generalized Hypergeometric Series

We shall investigate in this section certain properties of the function used in § 2, defined by

$$_1F_1(a;b;z) = 1 + \frac{a}{b.1}z + \frac{a(a+1)}{b(b+1).1.2}z^2 + \dots. \qquad (18)$$

Since we shall not have occasion to use any other function of hypergeometric type, we shall omit the suffixes. The function $M_{k,m}(z)$ defined by Whittaker† (confluent hypergeometric function) is connected with this function by the equation

$$M_{k,m} = z^{m+\frac{1}{2}}e^{-\frac{1}{2}z}{}_1F_1(\tfrac{1}{2}+m-k; 2m+1; z).$$

It may be noted here that $F(a;b;z)$ is a solution of the differential equation

$$z\frac{d^2y}{dz^2} + (b-z)\frac{dy}{dz} - ay = 0, \qquad (19)$$

as may easily be verified.

We require the asymptotic expansion of the function $F(a;b;z)$ for $|z|$ large, a and b remaining constant. This expansion is well known.

† Whittaker and Watson, *Modern Analysis*, 4th edition, p. 337.

We reproduce it here because of its importance in problems connected with Coulomb forces. The proof is similar to that given by Whittaker.†

We shall limit ourselves to the case when b is a positive integer, and z complex.

It is necessary for our purpose to express F as a contour integral. To do this we make use of the theorem that if m be any positive integer, then

$$\frac{1}{m!} = \frac{1}{2\pi i} \int_\gamma e^t t^{-m-1} \, dt, \tag{20}$$

where γ is any closed path encircling the origin once in an anti-clockwise direction. The proof is elementary.

Now F may be expressed in the following form:

$$F(a; b; z) = (b-1)! \sum_{n=0}^{\infty} c_n z^n / (b+n-1)!,$$

where c_n is the coefficient of x^n in the expansion of $(1-x)^{-a}$. Therefore, by means of (20), we have, putting $m = b+n-1$,

$$F(a; b; z) = \frac{(b-1)!}{2\pi i} \sum_{n=0}^{\infty} c_n z^n \int_\gamma e^t t^{-b-n} \, dt.$$

If we now choose our path γ so that on all points of it

$$|z/t| < 1, \tag{21}$$

then we may reverse the order of summation and integration, the series being convergent for all values of t. We obtain

$$F(a; b; z) = \frac{(b-1)!}{2\pi i} \int_\gamma \left(1-\frac{z}{t}\right)^{-a} e^t t^{-b} \, dt. \tag{22}$$

It will be noticed that, by virtue of (21), the path of integration γ must encircle the point $t = z$. We can therefore, without altering the value of the integral, deform γ into any closed path which encircles the points $t = 0$ and $t = z$.

It is further clear that the integrand is a single-valued function of t, if a cut be made between the points $t = 0$ and $t = z$.

In order to find the asymptotic expansion of (22) we deform γ into the path γ' shown in Fig. 4. Owing to the factor e^t in the integrand, those parts of γ' for which the real part of t is large and negative contribute very little to the integral. If we make the parts of γ' marked AB, CD, in Fig. 4 tend to an infinite distance from the imaginary axis,

then (22) may be replaced by the sum of the two integrals, one round the lower loop and the other round the upper. We set therefore

$$F(a;b;z) = W_1(a;b;z) + W_2(a;b;z), \tag{23}$$

where

$$W_1(a;b;z) \quad \frac{b-1)!}{2\pi i} \int_{\gamma_1} \left(1 - \frac{z}{t}\right)^{-a} e^t t^{-b} \, dt$$

and γ_1 comes from $-\infty$, encircles the origin in an anti-clockwise direction, and returns to $-\infty$. W_2 is given by the same integrand, and a path that encircles the point $t = z$. Making in W_2 the substitution

$$t - z = u$$
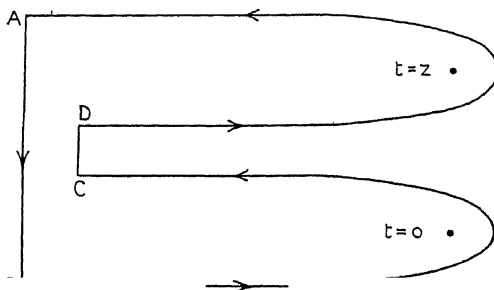
FIG. 4

the path transforms into γ_1 encircling the origin; we obtain

$$W_2(a;b;z) = \frac{(b-1)!}{2\pi i} \int_{\gamma_1} u^{-a} e^{u+z} \frac{du}{(u+z)^{-a+b}}.$$

The asymptotic expansions of W_1, W_2 may now be written down. We have

$$W_1 = \frac{(b-1)!}{2\pi i} (-z)^{-a} \int_{\gamma_1} \left(1 - \frac{t}{z}\right)^{-a} e^t t^{a-b} \, dt,$$

$$W_2 = \frac{(b-1)!}{2\pi i} (+z)^{a-b} e^z \int_{\gamma_1} \left(1 + \frac{t}{z}\right)^{a-b} e^t t^{-a} \, dt.$$

Expanding the brackets in the integrand, and making use of the theorem that†

$$\frac{1}{\Gamma(x)} = \frac{1}{2\pi i} \int_{\gamma_1} e^t t^{-x} \, dt,$$

† Whittaker and Watson, *Modern Analysis*, 4th edition, pp. 244–5.

we obtain

$$W_1 \sim \frac{\Gamma(b)}{\Gamma(b-a)}(-z)^{-a}G(a, a-b+1; -z)$$
$$W_2 \sim \frac{\Gamma(b)}{\Gamma(a)}e^z z^{a-b}G(1-a, b-a; z),$$

(24)

where G denotes the semi-convergent series

$$G(\alpha, \beta; z) = 1 + \frac{\alpha\beta}{z \cdot 1!} + \frac{\alpha(\alpha+1)\beta(\beta+1)}{z^2 \cdot 2!} + \cdots.$$

From (23) we obtain the asymptotic expansion of F.

4. Solution of the Equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right) + \left[\frac{8\pi^2 m}{h^2}\left(E - \frac{ZZ'\epsilon^2}{r}\right) - \frac{n(n+1)}{r^2}\right]L = 0. \quad (25)$$

This equation differs from Schrödinger's equation for the hydrogen atom only in the replacing of $-\epsilon^2/r$ by $+ZZ'\epsilon^2/r$. We are interested in the case of positive energy. The solution is well known, and is given here for reference.

If we make the substitution

$$L = r^n e^{ikr} F \qquad (k^2 = 8\pi^2 mE/h^2),$$

then (25) reduces to

$$r\frac{d^2 F}{dr^2} + [2ikr + (2n+2)]\frac{dF}{dr} - \left(\frac{8\pi^2 mZZ'\epsilon^2}{h^2} - ik(2n+2)\right)F = 0.$$

A further change of the independent variable from r to

$$z = -2ikr$$

reduces the equation to

$$z\frac{d^2 F}{dz^2} + (2n+2-z)\frac{dF}{dz} - (i\alpha+n+1)F = 0.$$

This equation is of the form (19) and has for a solution

$$F(i\alpha+n+1; 2n+2; z). \quad (26)$$

The other solution of (25) is not bounded at the origin.

The asymptotic expansion may be found from (24). If we take for the solution of (25)

$$L_n(r) = e^{-\frac{1}{2}\pi\alpha}\frac{|\Gamma(n+1+i\alpha)|}{(2n+1)!}(2kr)^n e^{ikr}F(i\alpha+n+1; 2n+2; -2ikr),$$

then the first term in the asymptotic expansion is

$$L \sim (kr)^{-1}\sin(kr - \tfrac{1}{2}n\pi + \eta_n - \alpha\log 2kr),$$
$$\eta_n = \arg\Gamma(n+1+i\alpha).$$

The Second Solution of (25). It may be shown† that if W_1, W_2 are the two functions defined in § 3, then

$$r^n e^{ikr} W_\mu(i\alpha+n+1; 2n+2; -2ikr),$$

where μ stands for 1 or 2, are independent solutions of (25). Since the asymptotic form of W is known, the solution with any required asymptotic form may be found.

The behaviour near the origin of the unbounded solution has been investigated by Sexl‡ for the case $n = 0$. He finds that the function

$$e^{ikr}\Gamma(1+i\alpha)W_2(1+i\alpha; 2; -2ikr),$$

which has the asymptotic form

$$e^{-ikr}(kr)^{i\alpha-1},$$

may be expanded in ascending powers of r, as follows:

$$\frac{-\exp[-i\alpha\log 2 + \tfrac{1}{2}\pi\alpha]}{kr\Gamma(1-i\alpha)} e^{-ikr}\left[1 + \sum_{n=0}^{\infty}(2ikr)^n c_n \log(2ikr+d_n)\right],$$

where

$$c_n = \Gamma(n-i\alpha)/\Gamma(n)\Gamma(n+1)\Gamma(-i\alpha),$$

$$d_n = \frac{1}{-i\alpha} + \frac{1}{-i\alpha+1} + \dots + \frac{1}{-i\alpha+n-1} + \frac{\Gamma'(-i\alpha)}{\Gamma(-i\alpha)} +$$

$$+ \frac{1}{n} - 2\left(\frac{1}{1} + \frac{1}{2} + \dots + \frac{1}{n}\right) + 2C,$$

$$C = 0.577\ldots.$$

† Whittaker and Watson, p. 343.
‡ *Zeits. f. Physik*, **56** (1929), p. 62. Cf. especially pp. 80 and 83.

IV

THE SPIN OF THE ELECTRON

1. The Magnetic Moment of an Atom

For some collision problems it is necessary to take account of the spin of the electron. We must therefore give a treatment of the spin suitable for use in such problems.

The hypothesis that an electron has an axis of symmetry, and thus a fourth degree of freedom, was introduced in 1925 before the discovery of the new quantum mechanics, in order to account for the four quantum numbers that were found to be necessary for the classification of atomic energy-levels. In the new quantum theory, methods for treating the spin were developed by Pauli† and Darwin.‡ Finally, Dirac,§ by means of a proper relativistic treatment of the wave equation, was able to show that the spin was a necessary consequence of the principle of relativity. In this chapter a treatment of the spin will first be given, which is equivalent to that of Pauli, and which is sufficient for all cases in which the spin influences the symmetry of the wave functions, but the interaction of the spin forces with the atomic fields can be neglected. This is the case in all collision problems where the velocity of the electrons considered is small compared with that of light. We shall also show the connexion between this treatment and the treatment based on Dirac's equation, and shall discuss a collision problem in which the spin forces cannot be neglected.

In Dirac's relativistic treatment of the spin the properties of the electron can be deduced from quite general assumptions. In the more elementary treatment, however, one takes the properties of the spin deduced from experiment, and describes them in the notation of wave mechanics. We begin with the fact, proved by the experiments of Gerlach and Stern, that an atom with one electron in an S state in the outer ring has a magnetic moment equal to $\epsilon h/4\pi mc$ (one Bohr magneton). For convenience, we shall refer to such an atom as a hydrogen atom.

We must first remark that if we are given a hydrogen atom of which the direction of the magnetic moment is not known, it is impossible

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† Pauli, *Zeits. f. Physik*, **43** (1927), 601.

‡ Darwin, *Proc. Roy. Soc.* A, **116** (1927), 227; see also Dirac, *Quantum Mechanics*, p. 132.

§ Dirac, *Proc. Roy. Soc.* A, **117** (1928), 610; also *Quantum Mechanics*, Chap. XIII.

by any conceivable experiment to discover this direction. This can be shown by the following argument. Suppose that an attempt were made to measure the field H outside an atom, in order to discover the direction of the magnetic moment. This might be done by shooting an electron past the atom and observing its deflexion. We can find the order of magnitude of this deflexion as follows: If the electron passes the atom at a distance r, the order of magnitude of H at points where the electron passes will be

$$H \sim M/r^3 \qquad (M = \epsilon h/4\pi mc).$$

The force on the electron is $\epsilon H v/c$. This force acts on the electron for a time of order of magnitude r/v, and produces, therefore, a momentum of order of magnitude $\epsilon H r/c$. The deflexion produced is thus $\epsilon H r/mcv$. This deflexion, to be observable, must be greater than the natural spreading of the beam of waves that represents the electron. If Δr is the breadth of this beam, then the spreading will be $h/mv\Delta r$. Thus we must have

$$\epsilon H r/mcv > h/mv\Delta r.$$

Putting in the value of H, we obtain

$$\Delta r/r > r/r_e \qquad (r_e = \epsilon^2/mc^2 \sim 2 \cdot 8 \times 10^{-13} \text{ cm.}).$$

Now r must be greater than the radius of the atom if the effect is to be observable. Thus we see that Δr is at least 20,000 times greater than r. The observation is therefore impossible.

We can determine the moment of a single atom only by means of a Stern-Gerlach experiment, and this experiment does not leave the atom undisturbed. The Stern-Gerlach experiment proves that a hydrogen atom in a magnetic field H must acquire additional energy equal either to $\pm MH$; the experiment, further, can separate the atoms having the two different energies. Since we have seen that the direction of the magnetic moment cannot be measured, *we must define the statement that the magnetic moment of an atom points in the direction* 1, *where* 1 *is a unit vector, as meaning that the atom has been passed through an inhomogeneous magnetic field H in the direction* 1, *and that the atom was in the deflected beam having energy* $-HM$.

We must now ask in what respect an atom that has been prepared in this way is different from any other atom. We wish to know whether any predictions can be made about its future behaviour that could not be made about an atom that had not been so prepared. We have seen that the direction of its magnetic moment cannot be measured. We can, however, put it through a second inhomogeneous magnetic field H' in a new direction 1', and observe whether the atom takes up energy

$\pm H'M$ in this new field. *From our knowledge of the way in which the atom has been prepared, it is possible to predict the probability that the atom will take up either of these energies.*† In the special case where **1** and **1′** refer to the same direction, it is of course certain that the energy will be $-H'M$. We shall now see how to calculate the probability in the more general case. To do this we must express our results in the notation of quantum mechanics.

We describe our knowledge of an atom whose magnetic moment has been orientated in the direction **1** by a Stern-Gerlach experiment, by a wave function

$$\chi_l(s).$$

The argument s of the wave function must refer to what is observable about the atom, namely, the energy that the atom would take up if passed into a second unhomogeneous magnetic field. We take therefore an arbitrary direction in space—say the z-axis—and denote by $H'Ms$ the energy that the atom would have if passed into a magnetic field H' in this direction. Then the probability that this energy will have a given value is $|\chi(s)|^2$; we know that χ must be zero unless s is ± 1. χ therefore has only two non-zero values, $\chi(+1)$ and $\chi(-1)$; the squares of the moduli of these give the probabilities that the energy shall have the values $\pm MH'$. It is clear that $|\chi_l(s)|^2$ will depend only on the angle between **1** and the z-axis.

If **1** lies along the z-axis, so that the energy is $-MH$, we have for χ

$$\left.\begin{array}{l}\chi(+1) = 0 \\ \chi(-1) = 1\end{array}\right\}. \tag{1}$$

Let us denote this function by $\chi_\beta(s)$. Similarly let χ_α be the corresponding function when **1** lies in the opposite direction, namely,

$$\left.\begin{array}{l}\chi_\alpha(+1) = 1 \\ \chi_\alpha(-1) = 0\end{array}\right\}. \tag{2}$$

We note that χ_α, χ_β defined in this way are both normalized and are orthogonal to each other.

The two wave functions χ_α and χ_β describe the two *stationary* states of the system—i.e. the two states in which the energy is known. The general state of the system will be described by a wave function

$$A\chi_\alpha + B\chi_\beta,$$

† Unless the field changes so abruptly that the atom passes from H to H' in a time small compared to the period of Larmor precession, no splitting will occur in the second experiment. The exact condition has been investigated by Rosen and Zener, *Phys. Rev.*, **40** (1932), 502.

where A and B are arbitrary complex constants satisfying the normalizing condition,

$$AA^* + BB^* = 1.$$

It can be shown† by arguments depending on invariance with respect to change of axes that if the atom is prepared with its magnetic moment lying in a direction specified by spherical polar angles θ, ϕ, and if also s refers to energies in a magnetic field along the z-axis ($\theta = 0$), then we have

$$B/A = -\cot \tfrac{1}{2}\theta \, e^{i\phi}, \tag{3}$$

and thus, neglecting an arbitrary phase,

$$A = -\sin \tfrac{1}{2}\theta, \qquad B = \cos \tfrac{1}{2}\theta \, e^{i\phi}.$$

The probability, therefore, that the atom will take up energy $-MH$ in the new field is $\cos^2 \tfrac{1}{2}\theta$, and that it will take up energy $+MH$ is $\sin^2 \tfrac{1}{2}\theta$.

The probability that the electron is at a given distance r from the nucleus will be approximately the same as it would be if the atom were not in a magnetic field, and will therefore be given by the square of the Schrödinger wave function

$$\psi(r) = (\pi a_0^3)^{-\frac{1}{2}} e^{-r/a_0}.$$

The complete wave function of the atom will therefore be the product

$$\psi(r)\chi(s).$$

This wave function will, however, be only approximately correct, because the charge distribution in an atom may well depend slightly on the orientation of the spin in a magnetic field.

We can, however (more accurately), describe the atom by a wave function

$$\psi(\mathbf{r}, s) \qquad (s = 1, -1). \tag{4}$$

The interpretation of this wave function is as follows: the function

$$|\psi(\mathbf{r}, s)|^2 \, dx\,dy\,dz \qquad (s = 1)$$

is the probability that the atom would have energy $+MH$ in a magnetic field along the z-axis, and that the electron would be found in a volume element $dx\,dy\,dz$.

The form of the function $\psi(\mathbf{r}, s)$ can only be found by applying the relativistic theory of the electron due to Dirac. It will be noticed that it is immaterial whether we write the wave function in the form (4), or whether we write *two* separate functions of $\mathbf{r}$, $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$. For velocities of the electron much less than c, both ψ_a and ψ_b are approximately solutions of Schrödinger's equation.

† Dirac, *Quantum Mechanics*, p. 132.

2. Magnetic Moment of the Electron

We have discussed so far only the magnetic moment of the atom. We shall not review here the evidence, derived from the anomalous Zeeman effect, from the gyromagnetic effect, etc., that the *electron* has a fourth degree of freedom, a magnetic moment $\epsilon h/4\pi mc$, and a mechanical moment $\frac{1}{2}h/2\pi$. We shall content ourselves with remarking that according to the Schrödinger theory the ground state of the hydrogen atom is not degenerate, and therefore, in order to account for the splitting in a magnetic field revealed by the Stern-Gerlach experiment, it is necessary to assume that the electron has a fourth degree of freedom.

The present evidence that electrons have a magnetic moment is derived from their behaviour when bound in stationary states in atoms. For the study of collision problems it is necessary to inquire what meaning can be attached to the magnetic moment of a free electron. In the first place, just as in the case of the atom, it is impossible to determine the moment by means of a magnetometer experiment. This can be shown by the following argument, due to Bohr.† Let us suppose that the position of the electron is known with an accuracy Δr and that we wish to determine the magnetic moment at a point distant r from it. It will not be possible to deduce from our measurement anything about the magnetic moment of the electron unless

$$\Delta r \ll r. \tag{5}$$

The field H that we wish to observe will be of order of magnitude

$$H \sim M/r^3.$$

If, however, the electron is in motion with velocity v, there will be a magnetic field due to its motion, of amount $\epsilon v/cr^2$; since we do not know v exactly we cannot allow for this field exactly. From our measurements, therefore, of the magnetic field, it will not be possible to find out anything about the magnetic moment of the electron, unless

$$M/r^3 \gg \epsilon \Delta v/cr^2,$$

where Δv is the uncertainty in our knowledge of v. Since by the uncertainty principle $\Delta r \Delta v > h/m$, this leads to

$$\Delta r \gg r,$$

which contradicts the inequality (5). We conclude therefore that it is not possible to measure the magnetic moment of an electron in this manner.

We shall now show that it is impossible, by means of a Stern-Gerlach

† Cf. Mott, *Proc. Roy. Soc.* A, **124** (1929), 440.

experiment, to determine the magnetic moment of a free electron, or to prepare a beam of electrons with the magnetic moments all pointing in the same direction. The argument is also due to Bohr.

In Fig. 5, a beam of electrons is supposed to travel parallel to the z-axis (i.e. perpendicular to the plane of the paper). The pole pieces of the magnet are shown, as are also the lines of force. The purpose of the experiment is to observe a splitting in the y-direction. The force on
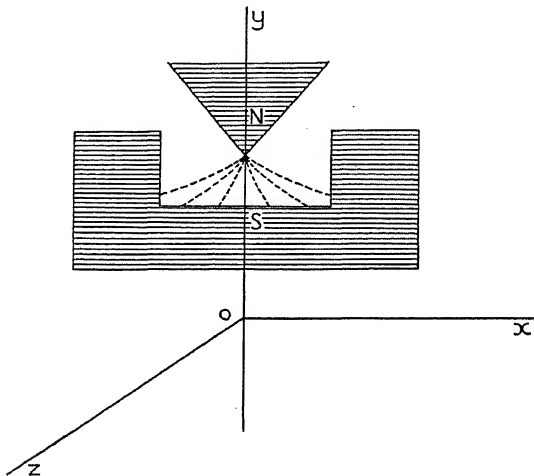
Fig. 5

an electron tending to split the beam will be

$$\pm M \frac{\partial H_y}{\partial y}. \tag{6}$$

Now all electrons will experience a force due to their motion through the field. Those moving in the plane Oyz will experience a force in the direction Ox. This force is perpendicular to the direction of the splitting, and its only effect will be to displace the beams to the right or to the left. However, electrons which do not move in the plane Oyz will experience a force in the direction Oy, because the lines of force in an inhomogeneous magnetic field cannot be straight, and there must be a component H_x of H along Ox. This force will have magnitude

$$\epsilon v H_x/c. \tag{7}$$

We can compare (7) with the force (6) tending to produce the splitting.

H_x at a point distant Δx from the plane Oyz will be equal to $\frac{\partial H_x}{\partial x}\Delta x,$

and since div H vanishes, this is equal to $-\dfrac{\partial H_y}{\partial y}\Delta x$. The quantities (6) and (7) therefore stand in the ratio

$$\frac{\epsilon h}{4\pi mc}\,\frac{\partial H_y}{\partial y} : \frac{\epsilon v}{c}\,\frac{\partial H_y}{\partial y}\,\Delta x.$$

Dividing through by common factors this becomes

$$1 : 4\pi\Delta x/\lambda, \tag{7.1}$$

where λ is the wave-length h/mv of the waves that represent the electrons. Suppose now that $\pm\Delta x$ is the distance from the plane Oyz of the two extremities of the beam. Since Δx must be greater than λ, it is clear that the two extremities of the beam will be deflected in opposite directions through angles greater than the angle of splitting, which we hope to observe.

To see now that it is impossible to observe any splitting, let us consider the trace that the beam would make on a photographic plate. Suppose that it were possible to use finer beams than is allowed by the uncertainty principle, so that the thickness Δy of the beam in the y-direction would be infinitely small. Before passing through the magnetic field, the cross-section of the beam would be as in Fig. 6 a. Afterwards, it would be as in Fig. 6 b, which shows the trace produced on a photographic plate. The tilting of the traces is produced by the Lorentz forces discussed above. If ABC, $A'B'$ are two lines parallel to Oy and distant λ apart, then by (7.1) we see that the tilting is so great that $AB > BC$. If $A\beta\gamma$ is drawn perpendicular to the traces, it follows that $A\beta > \beta\gamma$. But $A\beta < \lambda$, and hence $\beta\gamma$, the distance between the traces, is less than λ. Thus the maximum separation that can be produced is λ. But actually we cannot obtain a trace of breadth comparable with λ. Therefore it is impossible to observe any splitting.

From these arguments we must conclude that it is meaningless to assign to the free electron a magnetic moment. It is a property of the electron that when it is bound in an S state in an atom, the atom has a magnetic moment. When we consider the relativistic treatment of the electron due to Dirac, we shall see that this magnetic moment is not in general equal to $\epsilon h/4\pi mc$, unless the velocities of the electron within the atom are small compared with that of light (§ 3.3). A single electron bound in its lowest state in the field of a nucleus of charge $Z\epsilon$ gives, according to Dirac's theory, a magnetic moment†

† This formula is due to Breit, *Nature*, **122** (1928), 649. Cf. § 3.3 of this chapter.

$$\tfrac{1}{3}[1+2\surd(1-\gamma^2)]\epsilon h/4\pi mc \qquad (\gamma = 2\pi Z\epsilon^2/hc). \qquad (8)$$

The statement that a free electron has four degrees of freedom is on a different footing, for it is hardly conceivable that an electron in an atom should have four degrees of freedom, and a free electron three.
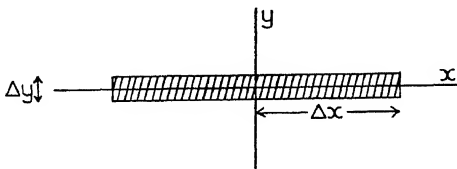
FIG. 6 a
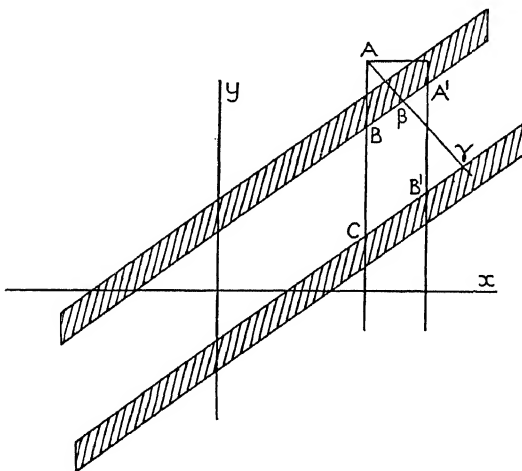
FIG. 6 b

It is interesting to inquire, therefore, whether there is any conceivable experiment by which this fourth degree of freedom could be detected. We wish to know whether it is possible to prepare a beam of electrons that is in some sense 'polarized', and whether it would be possible to detect this polarization.

There is at present no certain experimental evidence on this point; theoretical considerations show, however, that it is possible, in principle, both to prepare a polarized beam and to detect the polarization. Let us consider the following experiment.† A beam of atoms is prepared,

† This method of preparing a polarized beam of electrons was first suggested by Fues and Hellmann, *Phys. Zeits.*, **31** (1930), 465.

by means of a Stern-Gerlach experiment, with their axes all pointing in the same direction, say along the z-axis. Electrons are ejected from these atoms, by illuminating them with ultra-violet light. The beam of electrons obtained may be said to be polarized, for the following reasons: Assuming for the moment that the electron behaves like a small magnet, let us ask whether forces sufficient to eject the electron would be sufficient to alter appreciably the direction of the magnetic moment. The following purely classical considerations of the order of magnitude of the forces involved show that they are not, and so we may consider that the magnetic moments in the beam of ejected electrons all point in the same direction.†

If an electric field of intensity E acts on an electron for time t, the kinetic energy acquired is $\frac{1}{2}(E\epsilon)^2 t^2/m$. The energy that must be given to an electron to remove it from an atom is of order of magnitude $m\epsilon^4/h^2$. Thus to remove an electron from an atom the product of E and t must be of order of magnitude $Et \sim \epsilon m/h$. The average velocity of an electron in an atom is ϵ^2/h. The average couple acting on the electron magnet, due to its motion through the electric field E, will be of order

$$E \frac{\epsilon h}{mc} \frac{\epsilon^2}{h} \frac{1}{c},$$

which is equal to $E\epsilon^3/mc^2$. To change the orientation of the electron by an angle comparable with π, this couple must produce a change of angular momentum comparable with h. The time T necessary for this to occur is given by

$$T \frac{E\epsilon^3}{mc^2} \sim h,$$

which gives $\qquad\qquad ET \sim hmc^2/\epsilon^3.$

We deduce that $\qquad\qquad \dfrac{ET}{Et} \sim \left(\dfrac{hc}{\epsilon^2}\right)^2.$

Thus $\qquad\qquad\qquad T \gg t.$

It would be, however, meaningless to speak of a polarized beam, unless the fact that the beam is polarized could be detected in some way. This could be done if the beam were passed through a gas of ionized atoms, so that some of the electrons were captured. If the neutral atoms formed were shown by means of a Stern-Gerlach experiment to be polarized, then we should have a method of detecting the

† There is, of course, a small probability that the direction of the spin-axis is reversed, and the following discussions show this to be of order of magnitude $(1/137)^2$. There is no known method by means of which a completely polarized beam can be produced.

polarization. The argument used above about the order of magnitude of the forces involved indicates that this should be the case; a proper proof can, however, be given on the basis of Dirac's theory of the electron.

Another less direct but possibly more practical method of preparing and of detecting a polarized beam is discussed in § 4.1.

We see, then, that the spin of a free electron may be described by the same wave function $\chi_l(s)$ that was used before to describe the magnetic moment of an atom. The function

$$|\chi_l(s)|^2 \qquad (s = \pm 1)$$

gives the probability that, if the electron is prepared with its magnetic moment in the direction 1, then, if the electron be captured by an atom, and if that atom be passed into an inhomogeneous magnetic field, the energy of that atom will be either $\pm MH$. It is necessary to give to the square of the amplitude of the wave function this rather complicated interpretation, because it is not possible to measure the energy of an electron in a magnetic field, unless the electron is captured in an atom. It is further to be noted that, by the statement that an electron is prepared with its magnetic moment in a given direction, it is meant that the electron has been knocked off an atom that has been so prepared.

As in the case of the bound electron, an electron is completely described by a wave function

$$\psi(\mathbf{r}, s).$$

If the forces acting on the electron are so small that the direction of the spin remains constant throughout the experiment considered, then as before this function may be split up into the product

$$\psi(\mathbf{r})\chi(s),$$

when $\psi(\mathbf{r})$ is a solution of Schrödinger's equation. The form of $\psi(\mathbf{r}, s)$ when this is not the case can be found from Dirac's theory.

3. The Relativistic Wave Equation

As is well known, Dirac has been able to show that it is impossible to find a wave equation for an electron that is invariant with respect to a Lorentz transformation, and which is linear in the time differential, unless the electron be assumed to have a fourth degree of freedom. If one assumes this, it can be deduced that a hydrogen atom has a magnetic moment of the observed magnitude, without any further special assumptions. An understanding of the elements of Dirac's theory is

essential to the further development of our subject, and we shall there-fore give an outline of it here.

According to this theory, the electron is described by *four* wave functions

$$\psi_\lambda(x, y, z, t) \qquad (\lambda = 1, 2, 3, 4).$$

The probability that an electron will be in a volume-element $d\tau$ at time t is

$$\sum_{\lambda=1}^{4} |\psi_\lambda|^2 \, d\tau. \tag{9}$$

The four functions ψ_λ satisfy the simultaneous differential equations†

$$
\begin{aligned}
(p_0 + mc)\psi_1 + (p_1 - ip_2)\psi_4 + p_3\psi_3 &= 0 \\
(p_0 + mc)\psi_2 + (p_1 + ip_2)\psi_3 - p_3\psi_4 &= 0 \\
(p_0 - mc)\psi_3 + (p_1 - ip_2)\psi_2 + p_3\psi_1 &= 0 \\
(p_0 - mc)\psi_4 + (p_1 + ip_2)\psi_1 - p_3\psi_2 &= 0,
\end{aligned}
\tag{10}
$$

where

$$p_0 = -\frac{h}{2\pi i}\frac{1}{c}\frac{\partial}{\partial t} + \frac{\epsilon V}{c},$$

$$p_1 = \frac{h}{2\pi i}\frac{\partial}{\partial x} + \frac{\epsilon A_1}{c}, \text{ etc.}$$

V and $\mathbf{A}$ are scalar and vector potentials. We have to show that these equations describe an electron having the properties outlined in the preceding section.

We first note that if we wish to find a periodic solution, p_0 must be replaced by $(W + \epsilon V)/c$, W being the energy of the electron. Secondly, if we assume that the velocity of the electron is small compared with that of light, so that

$$W - mc^2 \ll W + mc^2,$$

then it is easy to see that ψ_3, ψ_4 both satisfy Schrödinger's equation. Further, if ψ is any solution of Schrödinger's equation, an approximate solution of (10) is

$$
\begin{aligned}
\psi_3 &= A\psi \\
\psi_4 &= B\psi \\
\psi_1 &= -\{B(p_1 - ip_2) + Ap_3\}\psi/2mc \\
\psi_2 &= -\{A(p_1 + ip_2) - Bp_3\}\psi/2mc.
\end{aligned}
\tag{11}
$$

A and B are arbitrary constants, and p_1, p_2, p_3 are to be interpreted as operators. It is clear that ψ_1, ψ_2 are much smaller than ψ_3, ψ_4 and can be neglected in the expression (9) for the charge density. Thus, if (9) is normalized to unity, and if we wish our four functions to be

† Darwin, *Proc. Roy. Soc. A*, **118** (1928), 654.

normalized also, we must have to this approximation

$$AA^* + BB^* = 1.$$

We wish to know, now, whether the solution of the equations (10) describes an electron with the spin properties that electrons are observed to have. It is known that the ground state of the hydrogen atom is degenerate, and that the energy splits into two in a magnetic field. We have to see whether this behaviour is predicted by the theory.

We see at once that the ground state is degenerate, the constants A and B being arbitrary. To find out what happens in a magnetic field, we must solve the equations (10) for an electron in the field of a nucleus and in a magnetic field H. We shall find that the degeneracy is then removed. If the magnetic field is along the z-axis, then one solution is given by (11) with

$$A = 0, \qquad B = 1.$$

This solution has energy $W_0 - MH$. We denote this solution by ψ_λ^{I}. The other solution ψ_λ^{II} has energy $W_0 + MH$ and is given by (11) with

$$A = 1, \qquad B = 0.$$

This is shown in § 4.

If the magnetic field does not lie along the z-axis, then the two solutions may either be found directly as above, or from a consideration of the way in which the functions transform under a change of axes.† If the direction of the magnetic field is given by the polar angles θ, ϕ, then the solution with energy $W_0 - MH$ is given by (11) with

$$A = -\sin\tfrac{1}{2}\theta, \qquad B = e^{i\phi}\cos\tfrac{1}{2}\theta.$$

The solution is therefore $A\psi_\lambda^{\text{I}} + B\psi_\lambda^{\text{II}}.$

This therefore is the wave function that describes an atom prepared with its magnetic moment pointing in the direction θ, ϕ. If the atom were then placed in a magnetic field along the z-axis, then clearly $|A|^2$ would give the probability that the atom should take up energy $+MH$, and $|B|^2$ the probability that it should take up energy $-MH$.

We have now shown that for slow electrons the Dirac treatment becomes identical with the non-relativistic Pauli-Darwin treatment. It is convenient to summarize here the two notations. In the Pauli-Darwin treatment an electron prepared with its axis in the direction 1 (polar angles θ, ϕ) is described by a wave function

$$\psi(x, y, z)\chi_l(s).$$

† Cf. Darwin, loc. cit.

ψ is the ordinary solution of Schrödinger's equation; HMs is the energy that the electron would have due to a magnetic field H along the z-axis. χ vanishes unless $s = \pm 1$ and then

$$\chi = e^{i\phi} \cos \tfrac{1}{2}\theta \qquad (s = -1),$$
$$\chi = -\sin \tfrac{1}{2}\theta \qquad (s = +1).$$

In Dirac's notation the electron is described by a wave function

$$\psi_\lambda(x, y, z) \qquad (\lambda = 1, 2, 3, 4).$$

ψ_1 and ψ_2 are negligible for slow electrons; ψ_3 and ψ_4 are multiples of ψ, and

$$\psi_3 = -\sin \tfrac{1}{2}\theta\, \psi,$$
$$\psi_4 = e^{i\phi} \cos \tfrac{1}{2}\theta\, \psi.$$

$|\psi_4|^2\, dx\, dy\, dz$ gives the probability that the electron is in the volume-element $dx\, dy\, dz$, and that the electron magnet would have energy $-MH$ in a magnetic field.

The fact that for slow electrons each of the functions ψ_3 and ψ_4 is approximately a solution of Schrödinger's equation provides a proof of the assumption made in § 2, that an electron can be ejected from one atom and captured by another atom without losing its spin direction. The spin direction will not in general change much unless the forces acting on the electron are such as to give it a velocity comparable with that of light.

3.1. *Treatment of the Equations when the Velocity of the Electrons is comparable with that of Light*

The exact solution of the equations (10) representing an electron moving in free space with momentum (p_1, p_2, p_3) and energy W has been given by Darwin,† and is

$$\psi_1 = -\frac{Ap_3 + B(p_1 - ip_2)}{mc + W/c} S \qquad \psi_2 = -\frac{A(p_1 + ip_2) - Bp_3}{mc + W/c} S$$
$$\psi_3 = AS \qquad \psi_4 = BS. \tag{12}$$

Here S denotes $\exp\{2\pi i(p_1 x + p_2 y + p_3 z - Wt)/h\}$, and A and B are arbitrary constants. The number of electrons per unit volume described by this solution is

$$(AA^* + BB^*)2W/(W + mc^2).$$

We must now ask what relationship the constants A and B in (12) have to the direction of the spin axis. We have seen *that for the case $v/c \ll 1$* this direction is given by the polar angles θ, ϕ, where

$$-B/A = \cot \tfrac{1}{2}\theta\, e^{i\phi}. \tag{13}$$

† Loc. cit.

For a fast electron, however, we have yet to define what is meant by the direction of the spin axis—i.e. how it could be measured.

Two methods are possible; we may either suppose that the 'observer' is moving with the electron, and inquire in what direction the spin of the electron is pointing relative to *his* axes; or we may suppose that the electron is brought nearly to rest by an electric field, and inquire what the direction of its spin axis is then. The first question has been considered by Darwin,† who finds that equation (13) defines the direction of the spin axis relative to the *moving* observer. The second, however, is the method by which the spin might be observed in practice; we find that equation (13) defines the direction of the spin when the electron has been reduced to rest. This may be seen as follows.

We confine ourselves to the case of an electron moving parallel to the z-axis, there being also an electrostatic field in this direction. The equations (10) reduce to two equations in ψ_2, ψ_4 and two equations in ψ_1, ψ_3. Eliminating ψ_2 between the first two of these, we obtain

$$\frac{2\pi i}{h}\left(\frac{W+\epsilon V}{c}-mc\right)\psi_4 - \frac{\partial}{\partial z}\left[\frac{h}{2\pi i}\left(\frac{W+\epsilon V}{c}+mc\right)\frac{\partial \psi_4}{\partial z}\right] = 0$$

and ψ_3 satisfies exactly the same equation. Thus, since ψ_3 and ψ_4 both satisfy the same boundary conditions, it follows that

$$\psi_3/\psi_4 = \text{const.}$$

Hence, as the velocity of the electron decreases, the ratio B/A does not change. Thus (13) gives the direction of the spin axis when the electrons are brought to rest by the field.

3.2. *Nature of an Unpolarized Beam.*

A *slow* unpolarized beam is one in which the electron spins point in all directions at random. It is not possible to represent an unpolarized beam by a single wave; each electron must be given its separate wave function, with different values of the constants A and B.

A 'fast' unpolarized beam is the beam produced from a slow beam by accelerating it by means of an electric field. It follows from the results of the last section that such a beam would appear unpolarized to a moving observer relative to whom the electrons were at rest.

We shall now show that a beam in which half the electrons have been prepared with their axes pointing in a given direction, and the other half with their axes pointing in the opposite direction, behaves like an unpolarized beam. To make the discussion definite, we shall

† *Proc. Roy. Soc.* A, **120** (1928), 628, § 5.

suppose that a beam of electrons travelling in the direction (l, m, n) passes into any electromagnetic field. The beam will be represented by a wave function $\psi_\lambda(x, y, z)\exp(-2\pi i Wt/h)$. In the part of space where the beam is before passing into the field, ψ_λ must have the form of a plane wave, moving in the direction (l, m, n) and polarized in some definite direction. Let (X, Y, Z) be some point in space where the beam arrives after it has passed the field, so that

$$P = \sum_\lambda |\psi_\lambda(X, Y, Z)|^2$$

gives the probability that an electron will be found at this point. We have to show that if P be averaged over all initial directions of the spin axis, the same result is obtained as by taking the average value of P for two opposite directions.

In the last section it was shown that a plane wave in which the spin axis points along the z-axis is represented by

$$\psi_3 = 0, \qquad \psi_4 = S,$$

and that a plane wave in which the spin axis points in the opposite direction is represented by

$$\psi_3 = S, \qquad \psi_4 = 0.$$

Let $\psi_\lambda^{\mathrm{I}}$, $\psi_\lambda^{\mathrm{II}}$ be the wave functions which have these forms in the part of space occupied by the incident wave. Then the wave function which describes an electron with spin initially in the direction (θ, ϕ) is

$$-\sin \tfrac{1}{2}\theta\, \psi_\lambda^{\mathrm{I}} + \cos \tfrac{1}{2}\theta\, e^{i\phi}\psi_\lambda^{\mathrm{II}}.$$

Thus $\quad P = \sin^2\tfrac{1}{2}\theta \sum_\lambda |\psi_\lambda^{\mathrm{I}}|^2 + \cos^2\tfrac{1}{2}\theta \sum_\lambda |\psi_\lambda^{\mathrm{II}}|^2 - \sum_\lambda \sin \theta \cos(\phi + \alpha_\lambda)D_\lambda,$

where we write $\qquad \psi_\lambda^{\mathrm{II}}(\psi_\lambda^{\mathrm{I}})^* = D_\lambda e^{i\alpha_\lambda}.$

If we take the opposite direction to θ, ϕ, namely,

$$\pi - \theta, \qquad \pi + \phi,$$

we obtain

$$P = \cos^2\tfrac{1}{2}\theta \sum_\lambda |\psi_\lambda^{\mathrm{I}}|^2 + \sin^2\tfrac{1}{2}\theta \sum_\lambda |\psi_\lambda^{\mathrm{II}}|^2 + \sum_\lambda \sin \theta \cos(\phi + \alpha_\lambda)D_\lambda.$$

The mean of these is $\qquad \tfrac{1}{2}\sum_\lambda [\,|\psi_\lambda^{\mathrm{I}}|^2 + |\psi_\lambda^{\mathrm{II}}|^2].$

Clearly the same result is obtained if P is averaged over all θ, ϕ.

3.3. *The Magnetic Moment of an Atom according to Dirac's Equation.*

Our purpose in this section is to show that an electron in the lowest quantum state, in the field of a nucleus of charge $Z\epsilon$, and a magnetic field H along the z-axis, has energy, according to Dirac's equation,

$$W_0 \pm HM,$$

where W_0 is the energy in the absence of a field, and

$$M = \frac{\epsilon h}{4\pi mc} \tfrac{1}{3}[1+2(1-\gamma^2)^{\frac{1}{2}}] \qquad (\gamma = 2\pi Z\epsilon^2/hc).$$

It will further be shown that, when the atom is in the state with energy $-HM$ (spin pointing along the z-axis), the wave function ψ_λ describing the electron is such that $\psi_3 = 0$.

The wave equation for the electron is (cf. equation 10)

$$\left[\frac{W+\epsilon V}{c} + \sum_{t=1}^{3} \alpha_t\left(p_t+\frac{\epsilon A_t}{c}\right)+\alpha_4 mc\right]\psi = 0,$$

where W is the energy, α_t, α_4 are the usual matrices, $V = Z\epsilon/r$, and A_t is given by

$$A_1 = -\tfrac{1}{2}Hy, \qquad A_2 = \tfrac{1}{2}Hx, \qquad A_3 = 0.$$

One can thus write the wave equation

$$(W+\epsilon V-U+c\sum \alpha_t p_t+\alpha_4 mc^2)\psi = 0,$$

where U is the perturbing energy due to the magnetic field, namely,

$$U = -\epsilon(\alpha_1 A_1+\alpha_2 A_2).$$

For the case $H = 0$, the lowest state is degenerate. There are two solutions, which we denote by ψ^{I} and ψ^{II}. If we write

$$f(r) = Ar^\beta e^{-r/a},$$

where

$$\beta = (1-\gamma^2)^{\frac{1}{2}}-1,$$

and A is so chosen that

$$4\pi \int\limits_0^\infty |f(r)|^2 r^2 \, dr = 1,$$

then these solutions, normalized to unity, are†

$$\left.\begin{aligned}
\psi_1^{\mathrm{I}} &= iNB\sin\theta\, e^{i\phi}f\\
\psi_2^{\mathrm{I}} &= -iNB\cos\theta\, f\\
\psi_3^{\mathrm{I}} &= 0\\
\psi_4^{\mathrm{I}} &= -Nf
\end{aligned}\right\} \qquad\qquad\qquad \text{(I)}$$

and

$$\left.\begin{aligned}
\psi_1^{\mathrm{II}} &= -iNB\cos\theta\, f\\
\psi_2^{\mathrm{II}} &= -iNB\sin\theta\, e^{i\phi}f\\
\psi_3^{\mathrm{II}} &= Nf\\
\psi_4^{\mathrm{II}} &= 0
\end{aligned}\right\}, \qquad\qquad\qquad \text{(II)}$$

where

$$B = \gamma[1+(1-\gamma^2)^{\frac{1}{2}}]^{-1}, \qquad (B^2+1)N^2 = 1.$$

It is easily seen that

$$\int \psi^{\mathrm{I}}\psi^{\mathrm{II}} \, dx\, dy\, dz = 0.$$

† Darwin, *Proc. Roy. Soc.* A, **118** (1928), 654.

For the energy values in a magnetic field we solve by the usual perturbation method. If therefore ΔW is the change of energy produced by the field, we obtain

$$\begin{vmatrix} \Delta W - U^{\mathrm{I,I}} & -U^{\mathrm{II,I}} \\ -U^{\mathrm{I,II}} & \Delta W - U^{\mathrm{II,II}} \end{vmatrix} = 0,$$

where $U^{\mathrm{I,II}} = \int \widetilde{\psi}^{\mathrm{I}} U \psi^{\mathrm{II}} \, dx\,dy\,dz$, etc.

It is easily seen that the non-diagonal elements $U^{\mathrm{I,II}}$ vanish; thus ψ^{I} and ψ^{II} are the correct zero-order wave functions, and $U^{\mathrm{II,II}}$ is the change of energy when the atom is in the state described by the wave function ψ^{II}.

We shall evaluate $U^{\mathrm{II,II}}$. We have

$$\widetilde{\psi}^{\mathrm{II}} \alpha_1 \psi^{\mathrm{II}} = \widetilde{\psi}_1 \psi_4 + \widetilde{\psi}_2 \psi_3 + \widetilde{\psi}_3 \psi_2 + \widetilde{\psi}_4 \psi_1$$
$$= 2N^2 B \sin\theta \sin\phi f^2.$$

Hence $\tfrac{1}{2}\epsilon H y \widetilde{\psi}^{\mathrm{II}} \alpha_1 \psi^{\mathrm{II}} = \epsilon H N^2 B \sin^2\theta \sin^2\phi \, r f^2.$

Similarly, we find that

$$-\tfrac{1}{2}\epsilon H x \widetilde{\psi}^{\mathrm{II}} \alpha_2 \psi^{\mathrm{II}} = \epsilon H N^2 B \sin^2\theta \cos^2\phi \, r f^2.$$

Thus, adding and integrating over all space, we have

$$U^{\mathrm{II,II}} = \epsilon H N^2 B \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^2 \, dr \sin^2\theta \, r f^2.$$

Evaluating this integral, we obtain

$$U^{\mathrm{II,II}} = \frac{\epsilon h H}{4\pi m c} \tfrac{1}{3}[1 + 2(1 - \gamma^2)^{\frac{1}{2}}],$$

which is the change of energy due to H when the atom is in the state II. Similarly we find that $U^{\mathrm{I,I}}$ is equal to *minus* the same quantity.

The factor $\tfrac{1}{3}[2(1-\gamma^2)^{\frac{1}{2}}+1]$ tends to 1 as $\gamma \to 0$. For uranium it is $0\cdot83$.

4. Scattering of a Beam of Fast Electrons by a Nucleus

If a beam of fast electrons is scattered by an atom the elastic scattering must be mainly nuclear [cf. Chap. IX, § 4.1 for an estimate of the screening effect of the electrons]. If the velocity of the electrons is comparable with that of light, we must use Dirac's relativistic wave equation to calculate the scattering. This has been done by Mott;† we shall only give the results here. The calculation is the relativistic generalization of that of Chapter III.

† *Proc. Roy. Soc.* A, **135** (1932), 429.

We require to calculate the 'effective cross-section' $I(\theta)\,d\omega$ for scattering into the solid angle $d\omega$, when electrons moving with velocity v are scattered by a nucleus of charge $Z\epsilon$. According to the classical theory, and also according to non-relativistic wave mechanics, one obtains

$$I(\theta) = (Z\epsilon^2/2mv^2)^2 \operatorname{cosec}^4\tfrac{1}{2}\theta.$$

Using Dirac's equation one obtains, for small θ, and all Z,

$$I(\theta) = (Z\epsilon^2/2mv^2)^2(1-v^2/c^2)\operatorname{cosec}^4\tfrac{1}{2}\theta.$$

For large angles, *and small Z*, one obtains

$$I(\theta) = (Z\epsilon^2/2mv^2)^2\left(1-\frac{v^2}{c^2}\right)\left(1-\frac{v^2}{c^2}\sin^2\tfrac{1}{2}\theta\right)\operatorname{cosec}^4\tfrac{1}{2}\theta.$$

For large angles and large Z, the scattering is not given by any simple formula. It has been calculated for gold, at a scattering angle of 90°, for various velocities. For details see loc. cit., eqs. (8.2) and (8.3).

Experiments on the nuclear scattering of fast particles have been carried out by Klemperer[†] and Neher.[‡] Neher finds that for aluminium the variation with angle and voltage agrees well with theory if the experimental results are multiplied by a constant factor of about 1·32. For scattering between the angles 95° and 172°, $v/c \sim 0\cdot6$, Neher finds that the factor

$$\int_{95}^{172} I(\theta)\sin\theta\,d\theta/Z^2$$

is not constant for different elements, being about 1·38 greater for gold than for aluminium.[§] This is in qualitative agreement with theory; for scattering at 90° only, the theoretical value of this ratio is about 2·1.

4.1. *Polarization of a Beam of Scattered Electrons.*

It was early suggested that a beam of electrons scattered from a target might be polarized, and that the polarization could be detected by scattering from a second target. The theory of the phenomenon has been investigated;[‖] if electrons are scattered from two targets B, C, more electrons should be scattered along CD than along CE. The effect predicted by theory is only large under the following conditions:

The targets must be thin, so that conditions of single scattering obtain.

[†] *Ann. d. Physik*, **3** (1929), 849.
[‡] *Phys. Rev.*, **38** (1931), 1321.
[§] We are indebted to Dr. Neher for informing us by letter of these results.
[‖] Mott, loc. cit.

The angles θ_1 and θ_2 must be comparable with $90°$.

The atomic number of the scattering nuclei must be large.

The velocity of the scattered electrons must be comparable with c. With gold, $\theta_1 = \theta_2 = 90°$, the maximum asymmetry is 16 per cent., and occurs for an energy of 127 kV.
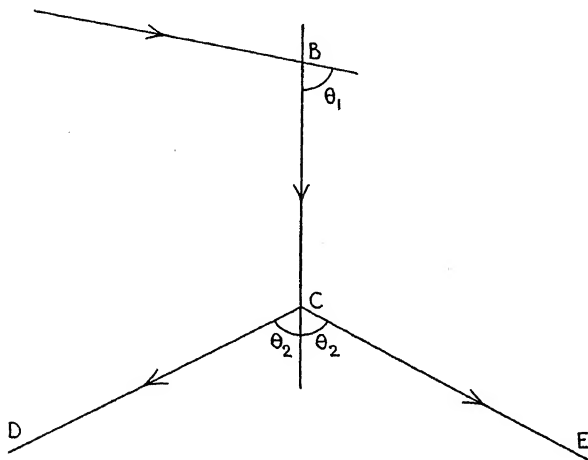
Fig. 7

Attempts to observe an effect of this type have been made by various workers. Of these, the only one in which the conditions were such that the theory predicts an effect is that of Dymond.† Dymond, using electrons of 79 kV. energy, obtained an asymmetry of 1·3 per cent. in the right direction; the amount demanded by the theory is 8 per cent. No explanation of the discrepancy has at present been given.

† *Proc. Roy. Soc.* A, **136** (1932), 638. Rupp, *Zeits. f. Physik*, **79** (1932), 642, has also recently investigated the phenomenon under these conditions; an effect of the order predicted by the theory is observed, but the maximum asymmetry is not observed at the energy predicted.

V

COLLISIONS BETWEEN TWO PARTICLES: NON-RELATIVISTIC THEORY

1. Introduction

In the first three chapters of this book we have discussed the motion of beams of electrons in various fields. If one assumes that the individual electrons of the beam do not interact with one another, the behaviour of the beam can be described by a wave function $\psi(x, y, z, t)$ in three-dimensional space, $|\psi|^2\, dxdydz$ giving the probability that an electron will be found, at time t, in the volume-element $dxdydz$. When we wish to discuss atomic systems in which it is necessary to take into account the interaction between two or more particles, this is no longer possible; a wave function which is a function of the coordinates of all the particles must be used. Examples of problems for the solution of which a wave function of this type must be used are: the treatment of atoms containing more than one electron; the hydrogen atom, when the finite mass of the nucleus is taken into account; the scattering of α-particles by light nuclei for which the recoil of the nucleus cannot be neglected; an exact theory, including inelastic collisions, of scattering of electrons by atoms.

In this chapter we discuss first the problem of the interaction between two unlike particles (§ 2). In § 3 we give a brief discussion of the stationary states possible for atoms or molecules containing two similar particles, and in §§ 4 and 5 we discuss the collision between similar particles, with and without spin. It may be emphasized here that if the particles are unlike, it is not necessary to take account of the spin, unless their velocities are comparable with that of light, in which case a relativistic theory must be used (Chap. XV). If, however, the particles are similar, one must take account of the spin even in a non-relativistic theory.

2. Interaction of Two Unlike Particles. Non-relativistic Theory without Spin

Let us suppose that the particles are an electron and a proton; our theory can then be applied to the problem of the hydrogen atom, and to the problem of the scattering of electrons by a hydrogen nucleus. As in the case of the one-body problem, the result of any experiment can be deduced from a wave function ψ. ψ will be a function of the

coordinates of both particles; if

$$\mathbf{r}_p = (x_p, y_p, z_p)$$
$$\mathbf{r}_e = (x_e, y_e, z_e)$$

are the coordinates of the proton and of the electron respectively, the wave function will be of the form

$$\psi(\mathbf{r}_e, \mathbf{r}_p; t).$$

The interpretation of this wave function is as follows: if $d\tau_e$ and $d\tau_p$ are two elements of volume situated at the points $\mathbf{r}_e$ and $\mathbf{r}_p$, then

$$|\psi(\mathbf{r}_p, \mathbf{r}_e; t)|^2 \, d\tau_p \, d\tau_e$$

is the probability that the proton is in the volume-element $d\tau_p$ and that the electron is in the volume-element $d\tau_e$, both at the instant of time t.

The wave function ψ satisfies Schrödinger's equation

$$-\frac{ih}{2\pi} \frac{\partial \psi}{\partial t} = \frac{h^2}{8\pi^2 m_p} \nabla_p^2 \psi + \frac{h^2}{8\pi^2 m_e} \nabla_e^2 \psi - V(\mathbf{r}_p, \mathbf{r}_e)\psi. \tag{1}$$

Here
$$\nabla_p^2 = \frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2}.$$

m_p, m_e are the masses of the proton and electron respectively; $V(\mathbf{r}_p, \mathbf{r}_e)$ denotes the potential energy of the pair of particles when the proton is at the point $\mathbf{r}_p$, and the electron at the point $\mathbf{r}_e$.

As an example, we shall obtain the solution which describes the motion of a hydrogen atom in field-free space. The potential energy function in this case is

$$V(\mathbf{r}_p, \mathbf{r}_e) = -\epsilon^2 / |\mathbf{r}_p - \mathbf{r}_e|.$$

As in the classical mechanics, the problem is separable; it is possible to discuss separately the motion of the centre of gravity, and of the line joining the particles. We make the substitution

$$(m_p + m_e)\mathbf{R} = m_p \mathbf{r}_p + m_e \mathbf{r}_e$$
$$\mathbf{r} = \mathbf{r}_p - \mathbf{r}_e, \tag{2}$$

so that $\mathbf{R}$ is the position of the centre of gravity of the two particles, and $\mathbf{r}$ denotes the length and direction of the line joining them. The operator

$$\frac{h^2}{8\pi^2 m_p} \nabla_p^2 + \frac{h^2}{8\pi^2 m_e} \nabla_e^2$$

transforms into†
$$\frac{h^2}{8\pi^2 M} \nabla_R^2 + \frac{h^2}{8\pi^2 m^*} \nabla_r^2,$$

where
$$M = m_p + m_e, \qquad m^* = m_p m_e / (m_p + m_e).$$

† See, for instance, Sommerfeld, *Wave Mechanics*, p. 27, where this transformation is treated in detail. See also Frenkel, *Wellenmechanik*, p. 131.

The wave equation (1) becomes, therefore,

$$-\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 M}\nabla_R^2\psi + \frac{h^2}{8\pi^2 m^*}\nabla_r^2\psi + \frac{\epsilon^2}{r}\psi. \qquad (3)$$

This equation is separable; that is to say, we can obtain a solution of the form

$$f_0(\mathbf{r}, t)g_0(\mathbf{R}, t). \qquad (4)$$

Substituting (4) in (3), we obtain the pair of equations

$$-\frac{ih}{2\pi}\frac{\partial f_0}{\partial t} = \frac{h^2}{8\pi^2 m^*}\nabla^2 f_0^{\,\prime} + \frac{\epsilon^2}{r}f_0 + Af_0$$

$$-\frac{ih}{2\pi}\frac{\partial g_0}{\partial t} = \frac{h^2}{8\pi^2 M}\nabla^2 g_0 - Ag_0,$$

where A is a constant. The substitution

$$f_0 = f\exp(+2\pi iAt/h)$$
$$g_0 = g\exp(-2\pi iAt/h)$$

leads to

$$-\frac{ih}{2\pi}\frac{\partial f}{\partial t} = \frac{h^2}{8\pi^2 m^*}\nabla^2 f + \frac{\epsilon^2}{r}f \qquad (5)$$

$$-\frac{ih}{2\pi}\frac{\partial g}{\partial t} = \frac{h^2}{8\pi^2 M}\nabla^2 g, \qquad (6)$$

and we may thus take ψ to be equal to fg, where f and g satisfy (5) and (6).

Equation (6) is the wave equation for a free particle of mass M; the solution $g(\mathbf{R}, t)$ describes the behaviour of the centre of gravity of the atom. The particular solution required depends on the experiment which it is wished to discuss. If, for instance, ψ is the wave function describing a beam of atoms, g must be the wave function for a beam of particles, which was found in Chap. I, § 4. If the position and velocity of the atom are known approximately, with errors subject to the uncertainty principle, then g must have the form of the wave packet described in Chap. I, § 9.

Equation (5) is the wave equation for a particle of mass m^* and charge ϵ moving in the field of a fixed nucleus. If we wish to describe a hydrogen atom in its normal state, f must be the first characteristic solution of this equation.

3. Theory of the Interaction between Two Similar Particles

(This section is intended to be a summary of the usual theory of the stationary states of systems containing two similar particles.)

We shall suppose first that the particles have no spin. A particle with no spin has only three degrees of freedom,† its state being completely

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† We do not wish to imply that the α-particle and carbon nucleus have 'really'

determined when its position in space is given. [This is of course not true of an electron, because its magnetic moment can point in any direction.] The helium nucleus (i.e. the α-particle) and the carbon nucleus are examples of this kind of particle; the evidence that this is the case is discussed below.

Before considering collision phenomena, we must remind ourselves of certain properties of the *stationary states* which are possible for molecules (He_2, C_2H_2, etc.) containing *two* such particles. If we wish to calculate the energy values which are possible for such a molecule, we proceed as follows: Let us take the case of the helium molecule He_2. We first assign a coordinate to each particle, R_1, R_2 for the two nuclei, and r_1, r_2, r_3, r_4 for the electrons. We then write down the Schrödinger equation for the system; this is of the form

$$(H - E)\psi = 0, \tag{7}$$

where ψ is a function of the coordinates of the six particles, and H is the usual operator. As is well known, bounded solutions ψ can only be found for a certain series of values of E, the 'eigenvalues', which we denote by

$$E_0, E_1, E_2, \ldots.$$

We expect these to be the possible values of the energy of the molecule. Actually, only *half* the predicted number are found to occur in nature— i.e. in the band spectrum of the molecule.† We must now examine the reason for this fact.

Apart from accidental degeneracies, which can in general be removed by electric and magnetic fields, there corresponds, to each discrete eigenvalue E_n of the energy, a unique wave function

$$\psi_n(R_1, R_2; r_1, r_2, r_3, r_4),$$

which is a solution of the differential equation (7). These solutions all have the property that they are *either* symmetrical in the coordinates

only three degrees of freedom—i.e. that they are not complex structures which can be split up into their component parts. We mean simply that in the experiments considered the probability of the internal structure of the nucleus being in any stationary state other than its normal state is negligible, and also that the normal state is non-degenerate; and thus, when the nucleus is at rest in free space, three coordinates are sufficient to specify its state.

In considering the collision between atoms moving with gas-kinetic velocities, or indeed with any energy less than the first resonance potential, the helium atom may be treated as a 'particle without spin' (cf. Chap. VIII, § 3.1).

† Cf. Kronig, *Band Spectra*, p. 94. The statement is only true if it is understood to refer to a given electronic state, because some of the theoretically possible electronic states do not occur, owing to the exclusion principle.

R_1, R_2, *or* they are antisymmetrical; that is to say, either

$$\psi_n(R_1, R_2; r_1...) = \psi_n(R_2, R_1; r_1...) \qquad \text{(symmetrical)},$$

or $\qquad \psi_n(R_1, R_2; r_1...) = -\psi_n(R_2, R_1; r_1...) \qquad$ (antisymmetrical).

This property is not an assumption about the wave functions; it is a deduction from the differential equation that the wave functions satisfy. The proof† depends on the assumption that the mass and charge of the two particles are exactly the same, so that the operator H is symmetrical in the coordinates of the two particles.

It can further be deduced from the wave equation, that if the molecule is in a state described by a symmetrical wave function, then no possible disturbance can bring the molecule into a state described by an antisymmetrical wave function. The converse is also true. This is true not only of the *stationary* states; if a system containing the two nuclei is in any state described by a symmetrical wave function, the wave function will remain symmetrical under any perturbation whatever; and vice versa. The proof‡ depends essentially on the assumption that, given any field, and two points P and P', the potential energy with the particles at rest at P and P' respectively does not depend on *which* particle is at P and *which* at P'. If the particles were very slightly different, in mass or in charge, then this would not be the case, and in general a perturbation (such as a collision) would give a finite, if small, probability for a transition from a symmetrical to an antisymmetrical state.

We have already seen that only half of the mathematically possible values of the energy of the molecule occur in nature. It is found, for the molecules C_2H_2 and He_2, that the energy values which occur are those for which the corresponding wave function is symmetrical in the coordinates of the nuclei. No reason is known at present why this should be so,§ and we must regard it simply as an experimental fact; it is, however, consistent with, but not demanded by, the laws of quantum mechanics that either only symmetrical or only antisymmetrical states should occur, because, as we have seen, these laws demand that a molecule that is once in a symmetrical state will never make a transition to an antisymmetrical state. The fact that only half the states are

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† The proof is given at the end of this section.

‡ Cf. Dirac, *Quantum Mechanics*, p. 200, or Mott, *Wave Mechanics*, p. 117.

§ Unless we regard the α-particle and the carbon nucleus as complex systems formed from a given number of electrons and protons; we can then deduce the symmetry properties of the nuclei from the corresponding properties of the electron and proton. However, such predictions are not always in agreement with experiment. (Cf. Kronig, loc. cit.: the outstanding exception is nitrogen.)

observed, and that the missing states do not appear under any disturbance, shows that the properties of any two helium or carbon nuclei must be absolutely identical. It also proves that the particles have no fourth degree of freedom (spin)—at any rate in their normal state, if they are complex particles.

We now pass on to the consideration of particles with spin, such as the electron, proton, and most nuclei. As we have seen in Chapter IV, such particles have a fourth coordinate s, the energy of the particle if passed into a magnetic field H along the z-axis being proportional to sH. For electrons and protons s can only have the values ± 1; for nuclei other than protons certain other values are allowed.† A particle with spin is thus specified by the coordinates $(\mathbf{r}, s)$. We shall denote this group of four coordinates by θ.

If we wish to calculate the energy-levels of a system containing two particles with spin, such as the helium atom, which contains two electrons, we are faced with the difficulty that the Hamiltonian for such a system is not known exactly,‡ the corrections introduced by the spin being of the same order of magnitude as the 'relativity corrections'. The assumption that this Hamiltonian exists leads, however, to important qualitative results in agreement with experiment about the number and order of magnitude of the energy-levels, and the possibility of transitions from one to another.

Let, then, H be the Hamiltonian of a system containing two similar particles with spin, let us say a helium atom. To find the energy-levels we must solve the wave equation

$$(H-E)\psi = 0.$$

There will as before be a series of energy-levels E_n for which bounded solutions can be obtained, and corresponding wave functions $\psi_n(\theta_1, \theta_2)$. The operator H must be symmetrical in the coordinates of the two particles; therefore, as before, the wave functions corresponding to every non-degenerate stationary state will be either symmetrical or antisymmetrical; that is to say, we shall have either

$$\psi_n(\theta_1, \theta_2) = \pm\psi_n(\theta_2, \theta_1).$$

† In the usual theory of hyperfine structure, a nucleus is assigned an angular momentum $ih/2\pi$ ($i = 0, \frac{1}{2}, 1,...$), and a magnetic moment $ig(i)\epsilon h/4\pi mc$, where $g(i)$ is a number of the order $1/1000$. The extra energy due to the interaction with the magnetic field H due to the electronic shell is $m_H H g(i)\epsilon h/4\pi mc$, where m_H is the component of i along H. Cf. for example Pauling and Goudsmit, *Structure of Line Spectra* (1930), p. 202.

‡ Cf. Chap. XV.

As before, transitions between states of opposite symmetry cannot occur under any perturbation.

For all particles that have been investigated, it is found that either only the energy-levels with antisymmetrical wave functions occur (electrons, protons) or only the energy-levels with symmetrical wave functions (α-particles, carbon or nitrogen nuclei). As we have seen already, this fact is consistent with wave mechanics, but not demanded by it.

The possibility of ascertaining whether a given energy-level observed experimentally has a symmetrical or antisymmetrical wave function, although we have no exact theory of the interaction of particles with spin, depends on the fact that the spin forces are small. We should expect the wave function describing any non-degenerate state of, say, the helium atom to be of the form, approximately,

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(s_1, s_2),$$

where ψ, to a very good approximation, is a solution of Schrödinger's equation for point electrons. To calculate the energy-levels of the atom one proceeds as follows. First one solves Schrödinger's equation for point electrons; the solutions are of course symmetrical or antisymmetrical in $\mathbf{r}_1$, $\mathbf{r}_2$. Both sets of energy-levels are found to occur; but the levels with antisymmetrical wave functions (orthohelium) are found on close resolution to be triplets. This is explained as being due to the spin; χ has four stationary states, three symmetrical, and one antisymmetrical; these are, to the zero-order approximation:

$$\chi_\alpha(s_1)\chi_\alpha(s_2), \qquad \chi_\beta(s_1)\chi_\beta(s_2),$$
$$\chi_\alpha(s_1)\chi_\beta(s_2)\pm\chi_\alpha(s_2)\chi_\beta(s_1).$$

For the definitions of χ_α, χ_β cf. Chap. IV, § 2. Thus, corresponding to every solution of Schrödinger's equation, there are four theoretically possible energy-levels; the fact that the observed parhelium-levels are singlets and the orthohelium-levels triplets shows that only wave functions occur which are antisymmetrical† in θ_1, θ_2.

In the case of the homonuclear diatomic molecules the procedure is

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† Particles for which only antisymmetrical wave functions can exist are said to satisfy the Fermi-Dirac statistics; particles for which only symmetrical wave functions can exist, the Einstein-Bose statistics. Particles which obey the Fermi-Dirac statistics obey also the 'exclusion principle', as can easily be shown. For if two such particles are in states described by wave functions ψ_a, ψ_b, then the wave function describing the pair of particles is

$$\psi_a(\theta_1)\psi_b(\theta_2)-\psi_a(\theta_2)\psi_b(\theta_1).$$

But if the two states are the same, this wave function vanishes; therefore the two particles cannot be in the same state.

essentially the same; we solve the Schrödinger equation, neglecting the spin of the nuclei. The splitting produced by the nuclear spin is too small to be observed directly; the spin multiplicity of a given state is revealed only through its statistical weight, which affects the relative intensity of certain of the rotational bands. (Cf. Kronig, *Band Spectra and Molecular Structure* (1930), pp. 94 et seq.; cf. also the article by Kallmann and Schuler, *Ergebnisse d. exakt. Naturwiss.*, **11** (1932), 156.)

3.1. *Proof that the Wave Functions describing Systems containing Two Similar Particles in a Non-degenerate Stationary State are either Symmetrical or Antisymmetrical in the Coordinates of the Particles.*

Let 1, 2 denote the coordinates of the particles; then $\psi(1, 2)$, the wave function, satisfies

$$H(1, 2)\psi(1, 2) - E\psi(1, 2) = 0, \tag{α}$$

where H is some operator which is symmetrical in the coordinates of the particles. Since we assume that the state is non-degenerate, ψ is the only bounded solution of (α).

Interchanging the coordinates 1 and 2 in (α), we obtain

$$[H(2, 1) - E]\psi(2, 1) = 0. \tag{β}$$

But since H is symmetrical in the coordinates of the particles, $H(2, 1)$ is equal to $H(1, 2)$. Hence from (β) we obtain

$$[H(1, 2) - E]\psi(2, 1) = 0. \tag{γ}$$

It follows from (γ) that $\psi(2, 1)$ is a solution of equation (α). But since $\psi(1, 2)$ is the only solution of (α) which is everywhere bounded, we must have

$$\psi(2, 1) = A\psi(1, 2),$$

where A is a constant. But it is clear that

$$\iint [\psi(1, 2)]^2 \, d\tau_1 \, d\tau_2 = \iint [\psi(2, 1)]^2 \, d\tau_1 \, d\tau_2,$$

and that neither integral is zero.

It follows that

$$A^2 = 1.$$

Hence, since all the quantities in these equations are real, we have

$$A = \pm 1.$$

This is what we set out to prove. We must emphasize that the proof only applies to non-degenerate states. States with unquantized (positive) energy are always degenerate. For such states the theorem is not true.

Reference. For the general theory of non-combining states, see Dirac, *Principles of Quantum Mechanics*, Chap. XI.

4. Collision of Two Identical Particles without Spin

We suppose first that the particles have no spin (α-particles). Imagine an experiment similar to that illustrated in Fig. 8. α-particles are fired with velocity v at a screen AB, and α-particles are also fired with equal and opposite velocity, at a screen CD. Apertures in the screens are opened and shut again, not necessarily at the same moment. Wave packets would pass through. Let these have wave functions

$$u(\mathbf{r}, t), \qquad v(\mathbf{r}, t)$$

both normalized to unity.† The problem before us is how to calculate the wave function at a time t after the collision. The simplest procedure would be to assign to the particles coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, where $\mathbf{r}_1$ is the

FIG. 8

coordinate of the particle which passed through AB, etc. Thus the wave function before the collision would be

$$u(\mathbf{r}_1, t)v(\mathbf{r}_2, t), \tag{8}$$

and the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$ after the collision would be determined by means of a wave equation of the type (1) and this initial condition. To interpret the wave function, one would assume $|\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2\, d\tau_1\, d\tau_2$ to be the probability of the first α-particle being in the volume-element‡ $(\mathbf{r}_1, d\tau_1)$ at time t and the second α-particle in the volume-element $(\mathbf{r}_2, d\tau_2)$. The probability of finding one or other of the particles at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is thus (omitting t)

$$\left[|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2 \right] d\tau_1\, d\tau_2. \tag{9}$$

This method of treating the problem cannot, however, be correct. The reason for this is that if we take the initial wave function (8), and suppose there to be electrons present also, then we obtain a finite probability of a molecule being formed, and moreover a finite pro-

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† i.e. such that $\int |u(\mathbf{r}, t)|^2\, d\tau = 1$.

‡ We use the notation $(\mathbf{r}, d\tau)$ to denote a volume-element at the point $\mathbf{r}$, and of volume $d\tau$.

bability for the formation of *any* of the mathematically possible stationary states. Now this is contrary to experiment; we know that for He_2 only the stationary states with wave functions symmetrical in the coordinates of the nuclei are found in nature. We know also that if a wave function is initially symmetrical, it must remain symmetrical for all time. Thus we shall obtain agreement with experiment if we make our initial wave function symmetrical in the coordinates of the two α-particles.

The only way in which we can combine the wave packets u and v together to form a symmetrical function is by taking for our initial wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = k[u(\mathbf{r}_1)v(\mathbf{r}_2) + u(\mathbf{r}_2)v(\mathbf{r}_1)], \qquad (10)$$

where k is some constant. We must consider now the interpretation of this wave function; the value that must be assigned to k will then become apparent.

Since initially the wave packets do not overlap, it follows that for any value of $\mathbf{r}_1$ for which $u(\mathbf{r}_1)$ is finite, $v(\mathbf{r}_1)$ vanishes. Thus at time $t = 0$,
$$u(\mathbf{r}_1)v(\mathbf{r}_1) = 0.$$

Hence we have, when ψ is given by (10) above,

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = k^2|u(\mathbf{r}_1)v(\mathbf{r}_2)|^2 + k^2|u(\mathbf{r}_2)v(\mathbf{r}_1)|^2. \qquad (11)$$

Now u is a function which vanishes except in the neighbourhood of the slit AB, and v vanishes except in the neighbourhood of CD. Thus $|\psi|^2$ vanishes unless $\mathbf{r}_1$ is near AB, and $\mathbf{r}_2$ near CD, or vice versa. Thus we cannot interpret $|\psi|^2 d\tau_1 d\tau_2$ as being the probability that the particle observed at AB is in the volume-element $(\mathbf{r}_1, d\tau_1)$, etc., because this latter probability is zero if $\mathbf{r}_1$ is near CD. We must interpret $|\psi|^2 d\tau_1 d\tau_2$ as the probability that one α-particle (either of the two) is in the volume-element $d\tau_1$, and the other in the volume $d\tau_2$. It is clear that (11) gives this probability correctly if we put k equal to unity.†

We adopt this interpretation, therefore, of *any* wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ describing two identical particles. We may note that if this interpretation is to make sense, $|\psi|^2$ must be symmetrical, i.e. we must have

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2.$$

There are *two* ways in which, at time $t = 0$, we can form a wave function with this property; the two possible wave functions are

$$u(\mathbf{r}_1)v(\mathbf{r}_2) \pm u(\mathbf{r}_2)v(\mathbf{r}_1).$$

† Note that this gives $\qquad \iint |\psi|^2 \, d\tau_2 \, d\tau_1 = 2.$
Wave functions for two identical particles ought therefore to be normalized to 2.

Thus we see that with the interpretation given above we *must* use either a symmetrical or an antisymmetrical wave function; if it were not that, for He₂, no antisymmetrical states occur in nature, we should not know which to use, and it would be impossible to make predictions by means of wave mechanics, in collision problems of this type.

Of course it is not *a priori* necessary to interpret ψ in this way; we could use the unsymmetrical wave function, $u(\mathbf{r}_1)v(\mathbf{r}_2)$, at time $t = 0$, and make the interpretation that $|\psi|^2\,d\tau_1 d\tau_2$ is the probability that a particular one of the two particles is at $\mathbf{r}_1$. The objection to this course is, as we have emphasized, that it leads to finite probabilities for the formation of molecules in antisymmetrical stationary states, which are not observed.

The use of the symmetrical wave function will give different scattering probabilities from those obtained using unsymmetrical wave functions. If we use the latter, the initial wave function is $u(\mathbf{r}_1)v(\mathbf{r}_2)$; after time t let the wave function be $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$. We have to make the interpretation that $|\psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2\,d\tau_1 d\tau_2$ is the probability that the particle that was originally at AB is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$, while $|\psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2\,d\tau_1 d\tau_2$ is the probability that the particle which was originally at AB is in the volume $(\mathbf{r}_2, d\tau_2)$, etc. Thus the probability that one particle is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is (cf. equation (9))

$$\{|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2\}\,d\tau_1 d\tau_2. \tag{12}$$

On the other hand, if we use the symmetrical wave function, the initial wave function is

$$u(\mathbf{r}_1)v(\mathbf{r}_2) + u(\mathbf{r}_2)v(\mathbf{r}_1)$$

and the wave function after time t is

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) + \psi(\mathbf{r}_2, \mathbf{r}_1, t), \tag{13}$$

and the probability that a particle is at $(\mathbf{r}_1, d\tau_1)$ and the other at $(\mathbf{r}_2, d\tau_2)$ is

$$|\psi(\mathbf{r}_1, \mathbf{r}_2, t) + \psi(\mathbf{r}_2, \mathbf{r}_1, t)|^2\,d\tau_1 d\tau_2, \tag{14}$$

i.e.

$$[\,|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 + |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2 + \psi(\mathbf{r}_1, \mathbf{r}_2)\psi^*(\mathbf{r}_2, \mathbf{r}_1) +$$
$$+ \psi(\mathbf{r}_2, \mathbf{r}_1)\psi^*(\mathbf{r}_1, \mathbf{r}_2)\,]\,d\tau_1 d\tau_2. \tag{15}$$

We have seen that the use of the symmetrical wave function (13) forbids us to assign a probability to the event of a particular α-particle being found in the volume $d\tau_1$—let us say, the α-particle which was originally in the neighbourhood of AB. If an α-particle is observed at a given point, it is in general impossible, by any conceivable experiment, to find out whether it is the α-particle which was originally at AB, or the other. Thus the wave function gives us no more information than can be obtained experimentally. It is only possible in principle to know

which α-particle is observed, if the path of the wave packet describing one α-particle does not overlap at any point with the path of the wave packet describing the other α-particle. It is in principle possible to devise such an experiment with slow α-particles ($8\pi\epsilon^2/hv \gg 1$). In Fig. 9 the shaded areas represent the paths of the two wave packets. It is clear that if a particle is observed at P it must be the one which was originally at AB. Hence it appears that in this case the symmetrical
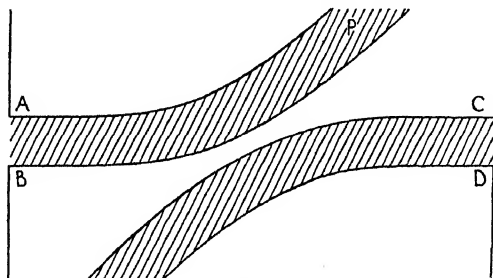
Fig. 9
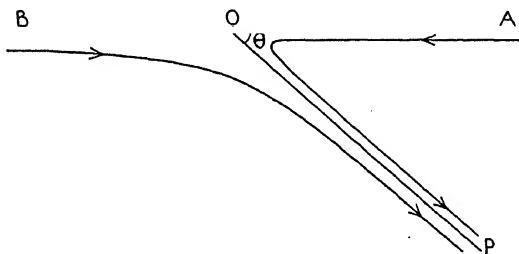
Fig. 10

wave function gives us less information than could be obtained experimentally. However, here the unsymmetrical wave function will give us the same probabilities of finding a particle as the symmetrical wave function, because the 'cross term' $\psi(\mathbf{r}_1, \mathbf{r}_2)\psi^*(\mathbf{r}_2, \mathbf{r}_1)$ in (15) vanishes for all $\mathbf{r}_1, \mathbf{r}_2$.

We must now consider in greater detail how to calculate the scattering when two particles collide. For purposes of calculation it is simplest to consider steady beams of infinite width. We therefore consider two beams moving with equal and opposite velocities $\frac{1}{2}v$ parallel to the z-axis. We require to find the number of scattered particles that will be observed travelling in the direction OP making an angle θ with BA. The particle may have been deflected through an angle θ from BO, or an angle $\pi - \theta$ from AO, as shown in Fig. 10.

We introduce coordinates $\mathbf{r}_1, \mathbf{r}_2$ to describe the two particles; we then transform to

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2).$$

We find† that a wave function can be obtained of the form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{R})\psi(\mathbf{r}).$$

In our case, since the centre of gravity is at rest, Ψ is a constant. ψ satisfies the equation

$$\nabla^2\psi + \frac{8\pi^2 m^*}{h^2}[\tfrac{1}{2}m^* v^2 - V(r)]\psi = 0, \tag{16}$$

where

$$m^* = \tfrac{1}{2}m$$

and $V(r)$ is the mutual potential energy of the particles. A solution $\psi(\mathbf{r})$ is obtained by the methods of Chapter II, having the form, for large r,

$$\psi \sim e^{ikz} + f(\theta)\, r^{-1}e^{ikr},$$

where e^{ikz} represents‡ the 'incident wave' (in $\mathbf{r}$ space), and $r^{-1}e^{ikr}$ the scattered wave. If the particles were distinguishable, one could use this wave function to describe the scattering; $|f(\theta)|^2$ would be proportional to the probability that the line joining the particles is deflected through an angle θ. Thus the number of particles scattered along OP would be proportional to

$$|f(\theta)|^2 + |f(\pi - \theta)|^2.$$

We must, however, use the symmetrical wave function

$$\psi(\mathbf{r}_1, \mathbf{r}_2) + \psi(\mathbf{r}_2, \mathbf{r}_1).$$

By interchanging $\mathbf{r}_1$ and $\mathbf{r}_2$, $\mathbf{r}$ is changed to $-\mathbf{r}$. r is therefore unaltered and θ is changed to $\pi - \theta$. The symmetrical wave function is therefore

$$e^{ikz} + e^{-ikz} + r^{-1}e^{ikr}[f(\theta) + f(\pi - \theta)]. \tag{17}$$

The incident wave may be written

$$2\cos kz = 2\cos k(z_1 - z_2);$$

the average value of $|\psi|^2$ for the incident wave is therefore 2, and so [cf. § 3, p. 69, footnote] the wave represents *one* particle per unit area in each beam. We deduce from (17) that the probability that a scattered particle will be found in a volume-element $d\tau_1$, and the particle with which it collided in the volume-element $d\tau_2$ is

$$\frac{1}{r^2}|f(\theta) + f(\pi - \theta)|^2\, d\tau_1\, d\tau_2,$$

† Cf. § 1 of this chapter.
‡ For the case of the Coulomb field the form of the incident wave is more complicated: cf. Chap. III, § 1.

where r is the distance between $d\tau_1$ and $d\tau_2$, and θ the angle that the line joining $d\tau_1$ and $d\tau_2$ makes with the z-axis.

It follows that the effective cross-section for a collision in which either particle is deflected into the solid angle $d\omega$ is

$$|f(\theta)+f(\pi-\theta)|^2\, d\omega. \tag{18}$$

The probability of scattering when one of the particles is initially at rest is easily obtained. In a given collision, the paths of the scattered particle and the knocked-on particle are at right angles. If an α-particle moving with velocity v strikes a stationary α-particle (He nucleus) the effective cross-section $I(\theta)\, d\omega$ for a collision in which a particle is scattered through an angle θ into a solid angle $d\omega$ is, from (18) (cf. Chap. VIII, § 5),

$$I(\theta)\, d\omega = |f(2\theta)+f(\pi-2\theta)|^2 4\cos\theta\, d\omega. \tag{19}$$

It is to be noted that (19) gives the probability that a particle will be observed moving in a direction making an angle θ with the direction of motion of the incident beam; the particle may be either a scattered α-particle from the incident beam, or a knocked-on helium nucleus. If a collision is observed, it is impossible to tell after the collision which is the incident particle and which the knocked-on particle, and, according to the wave mechanics, the question has no meaning.

4.1. *Coulomb Field.*

If the interaction between the particles may be represented with sufficient accuracy by the Coulomb field $V(r) = (Z\epsilon)^2/r$, then $f(\theta)$ is known, and is†

$$f(\theta) = \frac{Z^2\epsilon^2}{2m^*v^2}\operatorname{cosec}^2\tfrac{1}{2}\theta \exp[i\alpha\log(1-\cos\theta)+2i\eta_0],$$

where $\qquad m^* = \tfrac{1}{2}m, \qquad \alpha = 2\pi(Z\epsilon)^2/hv,$

and η_0 does not contain θ. From (19) we see that

$$I(\theta) = \left(\frac{Z^2\epsilon^2}{mv^2}\right)^2[\operatorname{cosec}^4\theta+\sec^4\theta+2\Phi\operatorname{cosec}^2\theta\sec^2\theta]4\cos\theta, \tag{20}$$

where $\qquad\qquad \Phi = \cos(\alpha\log\tan^2\theta).$

The corresponding formula‡ according to the classical mechanics is obtained from (20) by putting Φ equal to zero.

It will be noticed that formula (20) predicts that at 45° twice as many particles will be scattered as are predicted by the classical theory. The number scattered at a given angle according to formula (20) does

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† Cf. equation (16) of this chapter, and Chap. III, § 1.
‡ Cf. Rutherford, Chadwick, and Ellis, p. 262.

not tend to the number to be expected according to the classical theory, as $v \to 0$. The scattering *between any two* angles does, however, tend to the classical value, owing to the rapid oscillation between $+1$ and -1 of the function Φ for varying θ, when v is small and hence α is large.

Formula (20) has been verified experimentally for the scattering of α-particles in helium.† Rather slow α-particles have to be used, because it is only then that the assumption of inverse square law forces between the nuclei is sufficient. Cf. Chap. XV, § 5.

5. Collisions between Two Identical Particles with Spin

In the preceding section we have considered the collision between two similar particles which, firstly, have no spin, and, secondly, obey the Einstein-Bose statistics. In this section we consider the collision between particles, such as electrons and protons, which have spin—i.e. half a quantum of angular momentum, and obey the Fermi-Dirac statistics. The results may easily be generalized for particles with any number of quanta of angular momentum, and obeying either statistics, as is shown in § 6.

In the experiment considered at the beginning of the last section, if the particles have spin, the wave function which describes a particle must be a function of the spin coordinates. Let the particle which is passed through the slit AB have spin in the direction 1, so that the wave function describing the particle is‡

$$u(\mathbf{r})\chi_l(s).$$

Similarly let the wave function describing the other particle be

$$v(\mathbf{r})\chi_n(s).$$

Then since we must use an *antisymmetrical* wave function to describe the collision, the wave function at times before the collision is§

$$u(1)\chi_l(1)v(2)\chi_n(2) - u(2)\chi_l(2)v(1)\chi_n(1).$$

The wave function at a time after the collision, neglecting the small probability that the spins change their direction, is therefore

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \chi_l(1)\chi_n(2)\psi(1, 2) - \chi_l(2)\chi_n(1)\psi(2, 1). \tag{21}$$

The probability, therefore, that one particle is in the volume-element $(\mathbf{r}_1, d\tau_1)$ and the other in the volume-element $(\mathbf{r}_2, d\tau_2)$ is, at time t,

$$\sum_{s_1}\sum_{s_2} |\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2)|^2. \tag{22}$$

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† Chadwick, *Proc. Roy. Soc.* A, **128** (1930), 114; Blackett and Champion, *Proc. Roy. Soc.* A, **130** (1931), 380.

‡ Cf. Chap. IV, § 2, where definitions of χ_α, χ_β are given.

§ 1 stands for $\mathbf{r}_1$ or s_1, 2 for $\mathbf{r}_2$ or s_2.

Now,† if θ, ϕ be the polar angles of the direction 1 and θ', ϕ' of $\mathbf{n}$, we have

$$\chi_l(s) = -\sin\tfrac{1}{2}\theta\,\chi_\alpha(s) + \cos\tfrac{1}{2}\theta\,e^{i\phi}\chi_\beta(s).$$

Hence

$$\sum_s |\chi_l(s)|^2 = 1,$$

and

$$\sum_s \chi_l(s)\chi_n^*(s) = \sin\tfrac{1}{2}\theta\sin\tfrac{1}{2}\theta' + \cos\tfrac{1}{2}\theta\cos\tfrac{1}{2}\theta'\,e^{i(\phi-\phi')}.$$

It follows that (22) is equal to

$$|\psi(1,2)|^2 + |\psi(2,1)|^2 - [\psi(2,1)\psi^*(1,2) + \psi(1,2)\psi^*(2,1)]\times$$

$$\times[\sin^2\tfrac{1}{2}\theta\sin^2\tfrac{1}{2}\theta' + \cos^2\tfrac{1}{2}\theta\cos^2\tfrac{1}{2}\theta' + 2\cos\tfrac{1}{2}\theta\cos\tfrac{1}{2}\theta'\sin\tfrac{1}{2}\theta\sin\tfrac{1}{2}\theta'\cos(\phi-\phi')],$$

which reduces to

$$|\psi(1,2)|^2 + |\psi(2,1)|^2 - \tfrac{1}{2}[\psi(1,2)\psi^*(2,1) + \psi(2,1)\psi^*(1,2)](\cos\Theta + 1), \quad (23)$$

where Θ is the angle between the spin directions, namely,

$$\cos\Theta = \mathbf{1\cdot n}.$$

Thus (23) may be written

$$A\,|\psi(1,2) + \psi(2,1)|^2 + B\,|\psi(1,2) - \psi(2,1)|^2,$$

where

$$A = \tfrac{1}{4}(1-\cos\Theta), \qquad B = \tfrac{1}{4}(3+\cos\Theta).$$

Thus to obtain the probability of a given collision, one must calculate the probability using wave functions symmetrical in the space coordinates of the particles, and one must also calculate the probability using wave functions that are antisymmetrical. If the former probability is P_S and the latter P_A, then the actual probability is

$$\tfrac{1}{4}(1-\cos\Theta)P_S + \tfrac{1}{4}(3+\cos\Theta)P_A, \qquad (24)$$

where Θ is the angle between the spins of the two colliding particles. If this angle is unknown—i.e. if the two colliding beams are unpolarized —we must average (24) for all Θ. Since the average value of $\cos\Theta$ is zero, the probability is

$$\tfrac{1}{4}[P_S + 3P_A]. \qquad (25)$$

As an example, we shall suppose that a beam of electrons, of density such that one crosses unit area per unit time, collides with a single stationary free electron. It is required to calculate the probability, per unit time, that a collision takes place in which one of the particles, after the collision, moves in a direction lying in the solid angle $d\omega$ inclined at an angle θ to the direction of motion of the incident beam.

† Cf. Chap. IV, § 2.

Then† $P_S = \dfrac{\epsilon^4}{m^2v^4}[\mathrm{cosec}^4\theta + \sec^4\theta + 2\Phi\,\mathrm{cosec}^2\theta\sec^2\theta]4\cos\theta,$

and similarly,   (26)

$$P_A = \dfrac{\epsilon^4}{m^2v^4}[\mathrm{cosec}^4\theta + \sec^4\theta - 2\Phi\,\mathrm{cosec}^2\theta\sec^2\theta]4\cos\theta,$$

where $\Phi = \cos\left(\dfrac{2\pi\epsilon^2}{hv}\log\tan^2\theta\right).$

The actual probability is given by (24) or (25), according to whether or not the spin directions are known.

It will be noted that if the spins are in the same direction, we must use the antisymmetrical solution only. A consequence is that no electrons will be scattered, or knocked on, through an angle of 45°. If, on the other hand, the spins are antiparallel, so that Θ is 180°, then the number scattered is $\tfrac{1}{2}[P_S + P_A],$

which is equal to the number to be expected according to the classical theory.

In practice it is only possible to observe the scattering of a beam of electrons by stationary electrons when the 'stationary' electrons are bound in atoms. The incident beam must then have energy so great that the binding forces and motion of the atomic electrons may be neglected. If this is the case, we shall have

$$2\pi\epsilon^2/hv \ll 1.$$

The term Φ in (26) may therefore be replaced by unity, except at small angles, where the deviations from classical formulae are in any case small.

E. J. Williams‡ has compared the formulae (25), (26) with experiment by counting forked tracks in a Wilson chamber, using electrons of energies 20,000 volts. Good agreement with the theoretical formula was obtained.

The scattering of protons by hydrogen has been investigated by Gerthsen,§ and evidence in favour of the formula (25) obtained.

6. Collisions between Identical Nuclei

If a beam of atoms is fired into a gas composed of the same kind of atom, and if the energy of the beam is such that the distance of closest approach for scattering at a given angle is less than the radius of the

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† Cf. eq. (20).
‡ *Proc. Roy. Soc.* A, **128** (1930), 459.
§ *Ann. d. Physik*, **9** (1931), 769.

K ring, then the effect of the electrons on the collision may be neglected. The number of particles scattered will be given by the formula†

$$C_S P_S + C_A P_A.$$

where P_S, P_A are given by formulae (26), m and ϵ being equal to the mass and charge of the nuclei in question. C_S and C_A depend on the statistics obeyed by the nuclei, and also on the number of quanta of spin. The ratio $C_S : C_A$ is the same as the ratio of the intensities of the symmetrical to the antisymmetrical lines in the rotational band spectra of the diatomic molecule of the element concerned. Thus we should have

$$C_S : C_A = s_n/(s_n+1) \qquad \text{(Fermi-Dirac)},$$
$$= (s_n+1)/s_n \qquad \text{(Einstein-Bose)},$$

where $s_n h/2\pi$ is the angular momentum of the nucleus ($s_n = \frac{1}{2}$ for protons, zero for He, 1 for N_{14}, etc.). For further information about nuclear spins the reader is referred to Kronig, *Band Spectra* (1930), p. 96, or Kallmann and Schuler, *Ergebnisse d. exakt. Naturwiss.*, **11** (1932), 265.

† Cf. for example Sexl, *Zeits. f. Physik*, **80** (1933), 559.

VI

INHOMOGENEOUS DIFFERENTIAL EQUATIONS

IN this chapter methods are given for the solution of certain differential equations of the type
$$L\Psi = F,$$
where L is a linear differential operator of the second order, and F is a known function.

1. Ordinary Differential Equations. The General Solution

The general type of differential equation considered in this section is
$$\frac{d^2y}{dx^2} + 2p\frac{dy}{dx} + qy = f, \tag{1}$$
where p, q, f are known functions of x; however, by means of the substitution
$$y = \Psi \exp\left[-\int^x p\,dx\right]$$
the equation may be reduced to the form
$$\frac{d^2\Psi}{dx^2} + Q\Psi = F. \tag{2}$$

We shall therefore confine our attention to the equation (2).

Note that if, in the equation
$$\frac{d^2y}{dx^2} + \frac{2}{x}\frac{dy}{dx} + qy = f, \tag{1.1}$$
one makes the substitution $\quad y = x^{-1}\Psi,$
one obtains
$$\frac{d^2\Psi}{dx^2} + q\Psi = fx. \tag{2.1}$$

There are several methods of obtaining a solution of (2).

Method I.

We suppose that two independent solutions of the equation
$$\frac{d^2\psi}{dx^2} + Q\psi = 0 \tag{3}$$
are known. Let these solutions be ψ_1, ψ_2. Then it follows from (3) that
$$\frac{d}{dx}\left(\psi_1\frac{d\psi_2}{dx} - \psi_2\frac{d\psi_1}{dx}\right) = 0.$$
We can therefore multiply ψ_1, ψ_2 by constants in such a way that
$$\frac{d\psi_1}{dx}\psi_2 - \frac{d\psi_2}{dx}\psi_1 = 1 \qquad \text{(all } x\text{)}. \tag{4}$$

If ψ_1, ψ_2 are chosen so that (4) is satisfied, then

$$\Psi = \psi_1(x) \int_a^x \psi_2 F \, dx + \psi_2(x) \int_x^b \psi_1 F \, dx \tag{5}$$

is a solution of (2), as may be verified by substituting (5) in the equation (2). Further, since (5) contains two arbitrary constants a and b, (5) is the general solution of (2).

This method is discussed further in Courant-Hilbert, *Methoden d. mathematischen Physik*, 1924, p. 273.

Method II.

We suppose that one solution of equation (3) is known; denote this by ψ. Then if in equation (2) we make the substitution

$$\Psi = \psi\zeta$$

we obtain

$$\frac{d^2\zeta}{dx^2}\psi + 2\frac{d\zeta}{dx}\frac{d\psi}{dx} = F.$$

It follows that

$$[\psi]^2 \frac{d\zeta}{dx} = \int_\alpha^x F\psi \, dx', \tag{6}$$

and hence that

$$\Psi = \psi(x) \int_\beta^x [\psi(x')]^{-2} \, dx' \int_\alpha^{x'} F(x'')\psi(x'') \, dx'', \tag{7}$$

which is the required solution, containing the two arbitrary constants α and β.

Method I is the most suitable for the problems considered in this chapter. A third method is given in § 2 for certain differential equations.

2. Solution satisfying Boundary Conditions

In this section we shall show how to find the solution of the equation

$$\frac{d^2\Psi}{dx^2} + Q\Psi = F(x)$$

which satisfies certain boundary conditions. We shall take for Q and F functions satisfying the following conditions:

$$F(x) \to 0 \quad \text{as} \quad x \to \infty;$$

$F(x)$ bounded and differentiable in the range $0 < x < \infty$, except at the point $x = 0$, where there may be a pole of order x^{-1};

$$Q(x) = A - U(x),$$

where A is a constant, and U a function such that

$$xU(x) \to 0 \quad \text{as} \quad x \to \infty,$$

and $U(x)$ is bounded and differentiable, except at the point $x = 0$, where $U(x)$ may have a pole of the type $n(n+1)/x^2$ (n a positive integer or zero).

We shall impose on Ψ the two following boundary conditions:

(i) Ψ must be zero at the point $x = 0$. The indicial equation shows that one solution behaves like x^{n+1} and the other like x^{-n} near $x=0$; there will thus be one solution which vanishes at the origin.

(ii) The second boundary condition depends on the sign of A. If A is positive, we set

$$A = k^2$$

and choose Ψ so that $\qquad \Psi \sim \text{const.}\, e^{ikx}.$

If A is negative we choose Ψ so that Ψ shall be bounded as $x \to \infty$. We shall see that these two conditions determine Ψ completely, and that it is always possible to find Ψ satisfying these two conditions, for all A except in one special case.

We discuss first the case when A is positive. The equation that we have to solve is

$$\frac{d^2\Psi}{dx^2} + [k^2 - U(x)]\Psi = F(x). \tag{8}$$

Let ψ_1 be the solution, which vanishes at the origin, of

$$\frac{d^2\psi}{dx^2} + [k^2 - U(x)]\psi = 0. \tag{9}$$

Let ψ_1 be so normalized that†

$$\psi_1 \sim \sin(kx+\eta) \qquad (x \text{ large}).$$

Let ψ_2 be the solution of (9) such that

$$\psi_2 \sim k^{-1} \exp i(kx+\eta) \qquad (x \text{ large}).$$

Then ψ_1 and ψ_2 satisfy, for all x,

$$\psi_2 \frac{d\psi_1}{dx} - \psi_1 \frac{d\psi_2}{dx} = 1,$$

and hence (5) is the general solution of (8). The solution which vanishes at the origin is clearly

$$\Psi = \psi_1(x) \int_a^x \psi_2 F\, dx - \psi_2(x) \int_0^x \psi_1 F\, dx. \tag{10}$$

Both integrals converge as $x \to \infty$; thus the solution with the required form for large x is obtained by putting $a = \infty$. The form for large x is

$$\Psi \sim -k^{-1} e^{ikx+i\eta} \int_0^\infty \psi_1 F\, dx. \tag{11}$$

† Cf. Chap. II, § 1.

Thus a solution of the required form can always be found, provided the integrals

$$\int_0^\infty F(x)\exp(\pm ikx)\,dx$$

converge.

We shall now discuss the case when A is negative. Putting

$$A = -\gamma^2$$

we have to solve the equation

$$\frac{d^2\Psi}{dx^2} + [-\gamma^2 - U(x)]\Psi = F(x), \tag{12}$$

subject to the conditions, Ψ zero at the origin and bounded at infinity.

As before, let ψ_1 be the solution of

$$\frac{d^2\psi}{dx^2} + [-\gamma^2 - U(x)]\psi = 0, \tag{13}$$

which vanishes at the origin. In general, this solution, suitably normalized, will behave for large x like $\exp(+\gamma x)$. It is only for a certain series of values of γ (the eigenvalues) that ψ has the asymptotic form $\exp(-\gamma x)$.

If γ is not an eigenvalue, the required solution can be found as follows: Let ψ_2 be that solution of (13) which has asymptotic form

$$\psi_2 \sim \gamma^{-1}\exp(-\gamma x).$$

Then the required solution of (12) is

$$\Psi = \tfrac{1}{2}\left(\psi_1 \int_\infty^x \psi_2 F\,dx - \psi_2 \int_0^x \psi_1 F\,dx\right), \tag{14}$$

which tends to zero as x tends to infinity, if $F(x) \to 0$.

If γ is an eigenvalue, then the solution ψ_1 which vanishes at the origin has asymptotic form $\exp(-\gamma x)$; we must take for ψ_2 the solution which behaves like $\gamma^{-1}\exp \gamma x$; the solution of (12) which vanishes at the origin is

$$\Psi = \tfrac{1}{2}\left(\psi_1 \int_a^x \psi_2 F\,dx - \psi_2 \int_0^x \psi_1 F\,dx\right),$$

which for large x behaves like

$$\tfrac{1}{2}\left(e^{-\gamma x} \int_a^x \psi_2 F\,dx - e^{\gamma x}\gamma^{-1} \int_0^\infty \psi_1 F\,dx\right).$$

The first term may be shown to be bounded since $F \to 0$ as $x \to \infty$;

thus we can obtain a bounded solution if and only if

$$\int_0^x \psi_1 F \, dx \to 0. \tag{15}$$

A second method by which a solution of (12) may be obtained is that used in ordinary perturbation theory. We expand

$$F(x) = \sum_n a_n \psi_n(x), \tag{16}$$

$$\Psi(x) = \sum_n b_n \psi_n(x),$$

where the ψ_n are the normalized characteristic functions of the equation

$$\frac{d^2\psi_n}{dx^2} + [-\gamma_n^2 - U(x)]\psi_n = 0, \tag{17}$$

subject to the conditions that ψ should vanish at $x = 0$ and remain bounded at $x = \infty$.

The summation includes an integration over the continuous range of γ_n^2 ($-\gamma_n^2$ positive). There may not be any discrete values at all.

Substituting (16) into (12), multiplying by ψ_n, and integrating over all x, we obtain

$$b_n = a_n(\gamma_n^2 - \gamma^2)^{-1}.$$

If γ is one of the eigenvalues, say γ_m, then no solution vanishing at $x = 0$ and at $x = \infty$ exists unless $a_m = 0$; that is to say, unless

$$\int_0^\infty F(x)\psi_m(x) \, dx = 0,$$

which is the same condition as (15).

3. Partial Differential Equations

In this section we shall denote the position of a point in three-dimensional space by the Cartesian coordinates (x, y, z), or by the spherical polar coordinates (r, θ, ϕ), or by the vector $\mathbf{r}$.

We denote by L the operator

$$L = \nabla^2 + k^2 - U(r),$$

where $U(r)$ is a function such that

$$rU(r) \to 0 \quad \text{as} \quad r \to \infty.$$

Let $F(x, y, z)$ be a function such that $rF \to 0$ as $r \to \infty$. It is our purpose in this section to find a solution ψ of the equation

$$L\psi = F(x, y, z) \tag{18}$$

satisfying the boundary conditions

$$\psi \text{ everywhere finite;}$$

$$\psi \sim r^{-1}e^{ikr}f(\theta,\phi) \qquad \text{(large } r\text{);} \tag{19}$$

where $f(\theta,\phi)$ is some function which we must find.

To solve (18) we expand ψ and F in series of spherical harmonics. Let

$$P_n^m(\cos\theta) = \sin^m\theta \frac{d^m}{d(\cos\theta)^m}P_n(\cos\theta) \qquad (m \geqslant 0),$$

and let us use the convention that

$$P_n^m = P_n^{-m}.$$

We expand

$$F(x,y,z) = \sum_{n=0}^{\infty}\sum_{m=-n}^{m=+n}A_n^m(r)P_n^m(\cos\theta)e^{im\phi}.$$

Let the required solution ψ be

$$\psi(x,y,z) = \sum_n\sum_m B_n^m(r)P_n^m(\cos\theta)e^{im\phi}. \tag{20}$$

Substituting these expansions into (18), multiplying by

$$P_n^m(\cos\theta)e^{-im\phi}\sin\theta\,d\theta d\phi,$$

and integrating with respect to θ,ϕ over the surface of a sphere, we obtain

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dB_n^m}{dr}\right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2}\right)B_n^m = A_n^m(r). \tag{21}$$

Making the substitution $\qquad B_n^m = r^{-1}b_n^m,$

we obtain $\qquad \dfrac{d^2}{dr^2}b_n^m + \left(k^2 - U(r) - \dfrac{n(n+1)}{r^2}\right)b_n^m = rA_n^m(r),$

which is an equation of the type considered in §§ 1 and 2. The solution of (21) with the required boundary conditions is therefore, from (14),

$$B_n^m = -kL_n(r)\int_r^{\infty}H_n(r)A_n^m(r)r^2\,dr - kH_n(r)\int_0^r L_n(r)A_n^m(r)r^2\,dr, \tag{22}$$

where L_n, H_n are solutions of the equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dL}{dr}\right) + \left(k^2 - U(r) - \frac{n(n+1)}{r^2}\right)L = 0,$$

L_n being the solution bounded at the origin and so normalized as to have asymptotic form†

$$L_n \sim (kr)^{-1}\sin(kr - \tfrac{1}{2}n\pi + \eta_n),$$

and H_n being the solution with asymptotic form

$$H_n \sim (kr)^{-1}\exp i(kr - \tfrac{1}{2}n\pi + \eta_n).$$

(20) and (22) give us the solution that we require.

† Cf. Chap. II, § 1. The condition that L shall be bounded at the origin defines η_n.

For many purposes it is useful to express the solution as a definite integral

$$\psi = \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z')\, dx'dy'dz'. \tag{23}$$

If we write for K

$$K = -\frac{k}{4\pi} \sum_{n=0}^{\infty} (2n+1) L_n(r) H_n(r') P_n(\cos\Theta) \qquad (r' > r),$$

$$= -\frac{k}{4\pi} \sum_{n=0}^{\infty} (2n+1) H_n(r) L_n(r') P_n(\cos\Theta) \qquad (r > r'),$$

where

$$\cos\Theta = \cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi'),$$

then it may easily be shown that (23) is the required solution. For[†]

$$\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, P_n(\cos\Theta) P_n^m(\cos\theta) \exp(im\phi) = \frac{4\pi}{2n+1} P_n^m(\cos\theta') \exp(im\phi'). \tag{24}$$

It follows at once that (23) is the same as the solution given by (20) and (22).

3.1. *Asymptotic Form of the Solution.*

For large r, and fixed $\mathbf{r}'$,

$$K(\mathbf{r}, \mathbf{r}') \sim \frac{1}{4\pi} r^{-1} e^{ikr} \sum_{n=0}^{\infty} (2n+1) e^{-\frac{1}{2}in\pi + i\eta_n} L_n(r') P_n(\cos\Theta).$$

If we denote by $\mathfrak{F}(r, \theta)$ the function[‡]

$$\mathfrak{F} = \sum_{n=0}^{\infty} (2n+1) i^n e^{i\eta_n} L_n(r) P_n(\cos\theta),$$

then

$$K(\mathbf{r}, \mathbf{r}') \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \mathfrak{F}(r', \pi-\Theta).$$

The solution ψ therefore has asymptotic form

$$\psi \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \iiint \mathfrak{F}(r', \pi-\Theta) F(x', y', z')\, dx'dy'dz', \tag{25}$$

provided that the integral converges.

The equation $L\psi = F(x, y, z)$, where

$$L = \nabla^2 - \gamma^2 - U(r)$$

can be solved in a similar way. A bounded solution can always be obtained unless γ is an eigenvalue of the equation (cf. § 2)

$$L\psi = 0.$$

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† Whittaker and Watson, *Modern Analysis*, p. 328.
‡ Chap. II, eq. (16). The asymptotic form of $\mathfrak{F}$ is
$$\exp(ikz) + r^{-1} f(\theta) \exp(ikr).$$

4. Solution of the Equation

$$(\nabla^2 + k^2)\psi = F(x, y, z). \qquad (26)$$

This is a special case of the equation considered in the last section, the function $U(r)$ being put equal to zero. In this case

$$\mathfrak{F}(r, \theta) = \exp(ikz),$$

and therefore the *asymptotic form* of the solution ψ is, from (25),

$$\psi \sim -\frac{1}{4\pi} r^{-1} e^{ikr} \int\int\int \exp(-ik\mathbf{n}\cdot\mathbf{r}')F(x', y', z') \, dx'dy'dz', \qquad (27)$$

where $\mathbf{n}$ is a unit vector in the direction θ, ϕ, and so

$$\mathbf{n}\cdot\mathbf{r}' = r'[\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi - \phi')].$$

The solution ψ is

$$\psi = \int\int\int K(\mathbf{r}, \mathbf{r}')F(x', y', z') \, dx'dy'dz',$$

with

$$K = -\frac{1}{4\pi} \frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|},$$

as may be shown from equation (24), or directly as follows:

We make use of the theorem† that if f, g are any two bounded twice differentiable functions of x, y, z, and Ω any volume bounded by a closed surface Σ,

$$\int_{\Sigma} \left(f\frac{\partial g}{\partial n} - g\frac{\partial f}{\partial n} \right) dS = \int\int\int_{\Omega} (f\nabla^2 g - g\nabla^2 f) \, dxdydz. \qquad (28)$$

Here $\partial/\partial n$ denotes differentiation normal to dS *away from* the volume Ω; the surface integral on the left is to be taken over the surface Σ of Ω and the volume integral on the right throughout the volume of Ω. We apply this theorem by taking for f the solution ψ (assuming one to exist) of the equation (26) satisfying the boundary conditions. We take $\mathbf{r}'$ for our independent variable, so that f is $\psi(\mathbf{r}')$. For g we take $K(\mathbf{r}, \mathbf{r}')$ considered as a function of $\mathbf{r}'$, $\mathbf{r}$ being kept constant. For Ω we take the volume enclosed by two spheres ω_1, ω_2, both with their centres at the fixed point $\mathbf{r}$. The radius of ω_1 is to be ρ_1, and is finally to tend to infinity; the radius ρ_2 of ω_2 is finally to tend to zero. It will be seen that the point $\mathbf{r} = \mathbf{r}'$, at which K has a pole, is excluded from Ω.

We obtain

$$\int \left(\psi\frac{\partial K}{\partial n'} - K\frac{\partial \psi}{\partial n'} \right) dS' = \int\int\int (\psi\nabla^2 K - K\nabla^2\psi) \, dx'dy'dz'. \qquad (29)$$

† Jeans, *Electricity and Magnetism*, p. 160.

Now throughout Ω we have

$$\nabla^2 K = -k^2 K,$$

and

$$\nabla^2 \psi = -k^2 \psi + F(x', y', z').$$

Therefore the right-hand side of (29) is equal to

$$- \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') \, dx' dy' dz'. \tag{30}$$

The integral on the left-hand side of equation (29) can be split up into two parts: the integral over the outer boundary ω_1, and the integral over the inner boundary ω_2. Using the asymptotic expressions for ψ, K, it is easily seen that the first integral tends to zero as the radius of ω_1 tends to infinity. The expression

$$\int K \frac{\partial \psi}{\partial n'} \, dS'$$

tends to zero as the radius of ω_2 tends to zero; since, however, K has a zero at the centre of the circle, it follows that, as $\omega_2 \to 0$,

$$\int_{\omega_2} \frac{\partial K}{\partial n'} \psi \, dS' \to -\psi(\mathbf{r}) \int_{\omega_2} \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|^2} \, dS'$$

$$\to -\psi(\mathbf{r}).$$

Comparing this with (30), we have

$$\psi(\mathbf{r}) = \iiint K(\mathbf{r}, \mathbf{r}') F(x', y', z') \, dx' dy' dz',$$

which is what we set out to prove.

VII

<h1 style="text-align:center">SCATTERING BY A CENTRE OF FORCE</h1>

<p style="text-align:center">TREATMENT BY INTEGRAL EQUATION, AND
MISCELLANEOUS THEOREMS</p>

1. The Born Approximation

Our problem in this section is the same as that of Chapter II, namely, to calculate the scattering of a beam of particles by a field $V(r)$; we shall obtain an approximate formula which is only valid for fast particles, but which can be evaluated with much less labour than is required for the exact formula of Chap. II, eq. (17).

We have to solve the wave equation

$$\nabla^2\psi+[k^2-U(r)]\psi = 0, \tag{1}$$

where $\qquad k^2 = 8\pi^2 mE/h^2, \qquad U(r) = 8\pi^2 mV(r)/h^2,$

and where ψ must have the asymptotic form

$$\psi \sim e^{ikz}+r^{-1}e^{ikr}f(\theta). \tag{2}$$

We make use of the theorem, proved in Chap. VI, § 4, that the most general bounded solution of the equation

$$\nabla^2\psi+k^2\psi = F(x,y,z),$$

where $F(x,y,z) = F(\mathbf{r})$ is a known function, is

$$\psi = G(x,y,z)-\frac{1}{4\pi} \int \frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} F(\mathbf{r}')\,d\tau',$$

where G is the general solution of

$$\nabla^2 G+k^2 G = 0.$$

It follows that the general solution ψ of (1) will satisfy the integral equation

$$\psi = G-\frac{1}{4\pi} \int \frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} U(r')\psi(\mathbf{r}')\,d\tau'. \tag{3}$$

The expression on the right of (3) represents an outgoing wave; thus, in order that ψ may have the asymptotic form (2), we must choose

$$G = e^{ikz}.$$

To obtain $f(\theta)$ we require the asymptotic form of (3) for large r. Denoting by $\mathbf{n}$ a unit vector in the direction of $\mathbf{r}$, so that

$$\mathbf{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta),$$

we have $\qquad |\mathbf{r}-\mathbf{r}'| \sim r-\mathbf{n}\cdot\mathbf{r}'+\text{terms of order } 1/r,$

and hence from (3)

$$\psi \sim e^{ikz} - r^{-1}e^{ikr}\frac{1}{4\pi}\int e^{-ik\mathbf{n}\cdot\mathbf{r}'}U(r')\psi(\mathbf{r}')\,d\tau'. \tag{4}$$

Formulae (3) and (4) are exact. It is interesting to note that the scattered wave is that which would be produced if each element of volume scattered a wavelet of amplitude, at unit distance, $-2\pi mh^{-2}V(r)\,d\tau$ times the amplitude of the wave at that point.†

We may obtain a formula for $f(\theta)$ if we assume that the wave is not much diffracted by the scattering centre. We may then replace $\psi(\mathbf{r}')$ in the integral in (4) by the unperturbed wave function $\exp(ikz')$. This approximation is only valid for fast particles (cf. § 2 and Chap. IX).

We then obtain from (2) and (4), dropping the dashes,

$$f(\theta) = -\frac{1}{4\pi}\int \exp[ik(\mathbf{n}_0-\mathbf{n})\cdot\mathbf{r}]U(r)\,d\tau, \tag{5}$$

where $\mathbf{n}_0$ is a unit vector along the z-axis, so that $z = \mathbf{n}_0\cdot\mathbf{r}$. The integral may be evaluated by taking spherical polar coordinates α, β, the axis $\alpha = 0$ being taken in the direction of the vector $\mathbf{n}_0-\mathbf{n}$. We obtain

$$f(\theta) = -\frac{1}{4\pi}\int_0^{2\pi} d\beta \int_0^{\pi} \sin\alpha\,d\alpha \int_0^{\infty} r^2\,dr\,e^{iKr\cos\alpha}U(r),$$

where $\quad K = k|\mathbf{n}_0-\mathbf{n}| = 4\pi\sin\tfrac{1}{2}\theta/\lambda, \qquad \lambda = 2\pi/k = h/mv.$

Carrying out the integrations over α, β, we obtain

$$f(\theta) = -\frac{8\pi^2 m}{h^2}\int_0^{\infty}\frac{\sin Kr}{Kr}V(r)r^2\,dr. \tag{6}$$

This is the required formula; the intensity scattered into the solid angle $d\omega$ is $|f(\theta)|^2\,d\omega$.

If $V(r)$ is an atomic field, it is often convenient to transform (6) into an integral involving the charge density in the atom; if we denote by $-\epsilon\rho(r)$ the charge density at any point, we have

$$V(r) = -\frac{Z\epsilon^2}{r}+\epsilon^2\int\frac{\rho(r')\,d\tau'}{|\mathbf{r}-\mathbf{r}'|}. \tag{7}$$

Using the formula‡

$$\int\frac{\exp(i\mathbf{n}\cdot\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\tau' = \frac{4\pi}{|\mathbf{n}|^2}e^{i(\mathbf{n}\cdot\mathbf{r})},$$

† Cf. Mott, *Proc. Roy. Soc.* A, **127** (1930), 658.
‡ Cf. Chap. XI, § 1.1.

we obtain, substituting (7) in (5),

$$f(\theta) = \frac{8\pi^2 m}{h^2}\epsilon^2 \frac{Z - F(\theta)}{K^2}$$

$$- \frac{\epsilon^2}{2mv^2}[Z - F(\theta)]\operatorname{cosec}^2\tfrac{1}{2}\theta, \tag{8}$$

where
$$F(\theta) = 4\pi \int_0^\infty \rho(r)\frac{\sin Kr}{Kr}r^2\,dr. \tag{9}$$

The quantity F is known as the atomic scattering factor, and has been tabulated over a certain range of K for all elements.†

The formula (8) may be compared with the corresponding formula for X-rays. The intensity of X-rays scattered by an atom through an angle θ into a solid angle $d\omega$ is‡

$$\left[\frac{\epsilon^2}{mc^2}F(\theta)\right]^2 d\omega\,(1 + \cos^2\theta).$$

A simple explanation may be given of the similarity between these two formulae.§

1.1. Remarks about the Scattering as given by the Born Formula.

The scattered amplitude may be calculated either from formula (6) or (8). From either formula we see that the scattering is a function of $\sin\tfrac{1}{2}\theta/\lambda$ only, that is to say, of $v\sin\tfrac{1}{2}\theta$. This is not the case for the exact formula of Chapter II, and will therefore be true only under conditions (fast electrons) to which the Born formula can be applied.

It is clear from formula (6) that, if $V(r)$ tends to zero faster than r^{-3} as r tends to infinity, then $f(\theta)$ remains finite as θ tends to zero. This is true also of the exact formula (Chap. II, (17)) for $f(\theta)$.

For a given atom, the value of $f(\theta)$ for θ equal to zero is independent of v. $f(\theta)$ falls more steeply with increasing θ for large v than for small.

Since $F(\theta)$ tends to zero for increasing K, we see that for high velocities and large angles, $f(\theta)$ tends to $(Z\epsilon^2/2mv^2)\operatorname{cosec}^2\tfrac{1}{2}\theta$, so that the scattering is mainly nuclear, as one would expect. The non-occurrence of the phase factor (Chap. III, eq. (16)) in $f(\theta)$ is a consequence of our use of the Born approximation.

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† Cf. Chap. IX.
‡ Cf. Compton, *X-rays and Electrons*, p. 80, Chicago (1927).
§ Cf. Mott, loc. cit.

2. Connexion between the Born Formula and the Exact Formula for $f(\theta)$

The exact formula for $f(\theta)$ is $\big($cf. Chap. II, eq. (17)$\big)$

$$f(\theta) = \frac{1}{2ik} \sum_{n=0}^{\infty} (2n+1)[\exp(2i\eta_n)-1]P_n(\cos\theta). \tag{10}$$

The Born formula gives (cf. (6) above)

$$f(\theta) = -\frac{8\pi^2 m}{h^2} \int_0^{\infty} V(r)\frac{\sin Kr}{Kr}r^2\,dr. \tag{11}$$

In this section we shall investigate under what circumstances the formula (11) is a good approximation to (10). In Chap. II, § 2, an approximate expression for η_n was found, valid for η_n small. The formula obtained was

$$\eta_n \simeq -\frac{8\pi^2 mk}{h^2} \int_0^{\infty} V(r)[f_n(r)]^2 r^2\,dr, \tag{12}$$

where $$f_n(r) = (\pi/2kr)^{\frac{1}{2}}J_{n+\frac{1}{2}}(kr).$$

Since both (11) and (12) are obtained by treating $V(r)$ as a small perturbation, we should expect that, on substituting (12) in (10), we should obtain (11). That this is the case follows at once from the well-known expansion†

$$\frac{\sin Kr}{Kr} = \sum_n (2n+1)P_n(\cos\theta)[f_n(r)]^2,$$

if $\exp(2i\eta_n)-1$ in (10) is replaced by $2i\eta_n$.

The formula (12) often gives good results for η_n even when η_n is comparable with $\frac{1}{2}\pi$; one cannot then use the Born formula, but (12) may be substituted directly in (10) (cf. Chap. IX, § 5).

3. Classical Limit of the Quantum Theory Scattering Formulae

It is well known that if one makes h tend to zero in any formula of the quantum theory, one obtains the corresponding classical theory formula. It is interesting to show directly that this is so for our formula (Chap. II, eq. (17)) for the number of particles scattered by a field $V(r)$. We can see also under what conditions the number of particles scattered is the same on both theories.

We require first an expression for the number of particles scattered, according to the classical theory.

If we take the scattering centre at the origin, then the equation of

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† Watson, *Theory of Bessel Functions*, p. 363, eq. (3).

any orbit with energy E and angular momentum J is, in plane polar coordinates, r, ϕ,

$$\phi + \int^{r} \frac{\partial}{\partial J}[2m(E-V)-J^2/r^2]^{\frac{1}{2}} \, dr = 0. \tag{13}$$

If r_0 be the positive zero of

$$2m(E-V)-J^2/r^2,$$

and if α be the angle between the asymptotes of the orbit, then

$$\tfrac{1}{2}\alpha = - \int_{r_0}^{\infty} \frac{\partial}{\partial J}[2m(E-V)-J^2/r^2]^{\frac{1}{2}} \, dr. \tag{14}$$

θ, the angle of deflexion, is given by the equation

$$\theta = \pi - \alpha. \tag{15}$$

Thus from (14) and (15) we know the momentum J corresponding to a given deflexion θ.

Suppose now that we have a stream of particles whose velocity is v and that N cross unit area per unit time. Then the probable number of particles that cross per unit time a plane perpendicular to the direction of flight, with angular momentum between J and $J+dJ$, is

$$2\pi N J \, dJ/m^2 v^2.$$

The number of particles deflected between angles θ and $\theta+d\theta$ is, therefore,

$$\frac{2\pi N J}{m^2 v^2} \frac{dJ}{d\theta} \, d\theta,$$

J being given as a function of θ by (14) and (15). This number we have denoted by $2\pi N I(\theta)\sin\theta \, d\theta$ (cf. Chap. II, § 1). Thus we have

$$I(\theta) = \frac{J}{m^2 v^2} \frac{dJ}{d\theta} \frac{1}{\sin\theta}. \tag{16}$$

We now consider the quantum-theory formula. We require the solution of

$$\frac{d^2 L}{dr^2} + F(r)L = 0, \tag{17}$$

where

$$F(r) = \frac{8\pi^2 m}{h^2}(E-V) - \frac{n(n+1)}{r^2}.$$

Since we are investigating the case when $h \to 0$, we may suppose that F is large. With this assumption, the solutions of (17) are approximately†

$$F^{-\frac{1}{4}}\exp\left[\pm i \int^{r} F^{\frac{1}{2}} \, dr\right]. \tag{18}$$

† Jeffreys, *Proc. Lond. Math. Soc.*, Ser. 2, **23**, Part 6, or Chap. I, § 6, of this book.

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Since we are investigating the case when $h \to 0$, we may suppose that F is large. With this assumption, the solutions of (17) are approximately†

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† Jeffreys, *Proc. Lond. Math. Soc.*, Ser. 2, **23**, Part 6, or Chap. I, § 6, of this book.

We require the combination of these solutions that is finite at the origin. To find this, we note that $F(r)$ has a single zero, r_0 say, between $r = 0$ and $r = \infty$. $F(r)$ is negative for r less than r_0, positive for r greater than r_0. The solution (18) will therefore be oscillating for $r > r_0$, exponential for $r < r_0$. The solution that we require will clearly be the one that, for decreasing r, *decreases* exponentially as r becomes less than r_0. This solution is, to the same approximation as† (18),

$$L_n(r) \simeq F^{-\frac{1}{4}} \sin\left[\tfrac{1}{4}\pi + \int_{r_0}^{r} F^{\frac{1}{2}}\, dr\right]. \tag{19}$$

(19) is a valid approximation to $L_n(r)$ only in the range $r > r_0$. For large r, the asymptotic form of (19) is

$$\text{const.} \times \sin\left[\tfrac{1}{4}\pi + \int_{r_0}^{\infty} \{F^{\frac{1}{2}} - k\}\, dr + k(r - r_0)\right],$$

where $k^2 = 8\pi^2 mE/h^2.$

For the expression η_n (Chap. II, eq. (15)) therefore, we have, to the desired approximation,

$$\eta_n = \tfrac{1}{4}\pi + \tfrac{1}{2}n\pi - kr_0 + \int_{r_0}^{\infty} [F^{\frac{1}{2}} - k]\, dr. \tag{20}$$

This expression for η_n may be used for the calculation of the quantum-theory scattering in cases where η_n is large (cf. Chap. XIII, § 3.1).

To obtain the scattered amplitude $f(\theta)$ we now have to sum the series (Chap. II, eq. (17)),

$$f(\theta) = \frac{1}{2ik} \sum (2n+1)[\exp(2i\eta_n) - 1] P_n(\cos\theta). \tag{21}$$

Since the greatest part of the value of the series is contributed by large values of n, we replace $P_n(\cos\theta)$ by its asymptotic form‡ for large n

$$P_n(\cos\theta) \sim \left[\frac{2}{n\pi \sin\theta}\right]^{\frac{1}{2}} \sin[(n+\tfrac{1}{2})\theta + \tfrac{1}{4}\pi].$$

We note first that the series

$$\sum_n (2n+1) P_n(\cos\theta) \qquad (\theta \neq 0),$$

though divergent, is summable as the limit of a power series on its radius of convergence, and that the sum is zero. We may therefore subtract this series from (21). For $f(\theta)$ we obtain, therefore, the divergent

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† Cf. Jeffreys, loc. cit.
‡ See, for example, Jahnke-Emde, *Funktionentafeln*, p. 81.

but summable series

$$f(\theta) = \sum A(n)\{\exp[iB(n)] - \exp[iB'(n)]\}, \tag{22}$$

where

$$A(n) = -\frac{1}{2k}(2n/\pi \sin \theta)^{\frac{1}{2}},$$

$$B(n) = 2\eta_n + (n+\tfrac{1}{2})\theta + \tfrac{1}{4}\pi,$$

$$B'(n) = 2\eta_n - (n+\tfrac{1}{2})\theta - \tfrac{1}{4}\pi.$$

To sum such a series as

$$\sum_n A(n)\exp[iB(n)] \tag{23}$$

we inquire whether there is any value of n for which

$$\frac{dB(n)}{dn} = 0.$$

If there is any such value, n_0 say, then in the neighbourhood of n_0 there will be a large number of terms of the series over which $\exp[iB(n)]$ is not oscillating. Thus effectively all of the sum of the series comes from this region. (23) may then be replaced by

$$A(n_0)\exp[iB(n_0)] \int_{-\infty}^{+\infty} \exp\{i\beta(n-n_0)^2\}\, dn,$$

where

$$\beta = \frac{1}{2}\left(\frac{d^2B}{dn^2}\right)_{n=n_0}.$$

Evaluating the integral, we obtain

$$A(n_0)(\pi/i\beta)^{\frac{1}{2}}\exp[iB(n_0)]. \tag{24}$$

We now inquire whether the differential coefficient of $B(n)$ or $B'(n)$ does in fact vanish for any positive value of n. The condition is

$$2\frac{\partial}{\partial n}\int_{}^{\infty} [F^{\frac{1}{2}} - k]\, dr + \pi \pm \theta = 0$$

for B and B' respectively. Putting

$$nh/2\pi = J,$$

this condition reduces to

$$\int_{}^{\infty} \frac{\partial}{\partial J}[2m(E-V) - J^2/r^2]^{\frac{1}{2}}\, dr + \tfrac{1}{2}\pi \pm \tfrac{1}{2}\theta = 0. \tag{25}$$

If we take the negative sign we obtain equation (14), giving the classical angular momentum J of an electron scattered through an angle θ. One can easily see that if one takes the positive sign there is no positive J satisfying the equation. Thus in (22) the sum of the second series is

much greater than the sum of the first, and we have for $f(\theta)$

$$f(\theta) = -\sum_n A(n)\exp[iB'(n)],$$

which reduces, by (24), to

$$-A(n_0)(\pi/i\beta)^{\frac{1}{2}}\exp[iB'(n_0)],$$

where $hn_0/2\pi$ is the root of (25). For β we have

$$\frac{h}{2\pi}\frac{\partial^2}{\partial J^2}\int^\infty [2m(E-V)-J^2/r^2]^{\frac{1}{2}}\,dr,$$

which reduces by (25) to

$$\frac{h}{4\pi}\frac{\partial\theta}{\partial J}.$$

Putting in the value for $A(n_0)$ we obtain

$$|f(\theta)|^2 = J\frac{\partial J}{\partial\theta}\Big/m^2v^2\sin\theta,$$

which is the classical formula for $I(\theta)$.

We see that the condition for classical scattering at a given angle θ is that n_0 should be large, where n_0 is the value of n for which

$$\frac{\partial\eta_n}{\partial n} = \tfrac{1}{2}\theta,$$

and that η_n should also be large for this value. Compare the condition of validity of Born's formula, which is that η_n shall be small for all n.

GENERAL THEORY OF ATOMIC COLLISIONS

IN Chapters II and III we discussed the scattering of a stream of particles by a centre of force. The great majority of collision phenomena, however, involve some reaction of the scattered particle on the scatterer. We shall now develop a more general theory applicable to such problems as the following:

(1) The excitation of atoms and molecules by electron impact.

(2) The excitation of vibration and rotation of molecules by the impact of other molecules.

(3) The transfer of excitation between two atoms or molecules on collision.

(4) The excitation of atomic nuclei by α-particles or protons.

In all these cases there is a direct energy interchange between the relative translational motion and the internal motion of the colliding systems. There is no transfer of *particles* between the colliding systems on impact; this, however, occurs in a number of other types of collision which are of equal importance. These 'rearrangement' collisions include the following:

(1) The capture of electrons from atoms by positively charged particles.

(2) Emission of protons from atomic nuclei, with resultant capture of the exciting α-particle.

(3) Collisions of two molecules, resulting in a redistribution of electrons and nuclei.

(4) Collisions of electrons with atoms, in which exchange of particles takes place between the incident beam and the scattering atom, the incident electron being captured and the atomic electron ejected.

Since one cannot distinguish experimentally between the scattered and ejected electrons, and since, moreover, the wave function used must be antisymmetrical in the coordinates of these two, this type of problem requires a somewhat different treatment to the other three. The particular case of the collision of two similar particles, which may be reduced to a one-body problem, has already been considered in Chapter V.

In what follows, we shall distinguish the two types of collision by the terms 'direct' and 'rearrangement' inelastic collision.

Owing to the complexity of the phenomena, it is necessary, except in very special cases, to use approximate methods of treatment. For collisions in which the relative velocity of the colliding systems is large compared with the velocities of their internal motion, there is no difficulty in obtaining an accurate approximation ('Born's approximation'); but under other circumstances no general method has yet been developed, and special methods must be used for particular problems.

1. The Collisions of Electrons with Hydrogen Atoms. Born's Approximation

In order to make clear the method which must be employed in dealing with inelastic collisions, we will first consider the simplest type of collision which occurs in practice, that of electrons with hydrogen atoms. The mass of the electron is small compared with that of the proton, and the motion of the latter in the collision can be neglected.

We consider a beam of electrons falling on a hydrogen atom initially in the normal state. The intensity of the beam is such that one electron crosses unit area per unit time. We have to find the number of electrons that are scattered per unit time through an angle θ into a solid angle $d\omega$ after having excited the atom into its nth state. This number, $I_n(\theta) \, d\omega$, has the dimensions of an area and will be called the differential cross-section for scattering into the solid angle $d\omega$. The total cross-section Q_n corresponding to the excitation will be obtained by integrating over all angles, so that

$$Q_n = \int_0^{2\pi} \int_0^{\pi} I_n(\theta) \sin\theta \, d\theta d\phi. \tag{1}$$

The wave equation for the system of incident electron and atom is

$$\left[\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) + E + \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}} \right] \Psi = 0, \tag{2}$$

where the incident electron is distinguished by the suffix 1, the atomic electron by the suffix 2. The energy E is the sum of the energy E_0 of the atomic electron in its ground state and of the kinetic energy $\frac{1}{2}mv^2$ of the incident electron.

We may expand the function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \left(\sum_n + \int \right) \psi_n(\mathbf{r}_2) F_n(\mathbf{r}_1), \tag{3}$$

where the functions $\psi_n(\mathbf{r})$ are the proper functions for the hydrogen atom, satisfying

$$\left(\frac{h^2}{8\pi^2 m} \nabla^2 + E_n + \frac{\epsilon^2}{r} \right) \psi_n = 0. \tag{4}$$

The integral sign denotes integration over the functions of the continuous spectrum.

Substituting (3) in (2) and using (4), we obtain

$$\left(\sum_n + \int\right)\psi_n(\mathbf{r}_2)\left\{\frac{h^2}{8\pi^2 m}\nabla^2 + E - E_n\right\}F_n(\mathbf{r}_1) = \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1}\right)\Psi(\mathbf{r}_1, \mathbf{r}_2). \quad (5)$$

Multiplying both sides of this equation by $\psi_n^*(\mathbf{r}_2)$ and integrating over the coordinate space of the atomic electron, we obtain

$$\left\{\frac{h^2}{8\pi^2 m}\nabla^2 + E - E_n\right\}F_n(\mathbf{r}_1) = \int \left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1}\right)\Psi(\mathbf{r}_1, \mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\,d\tau_2. \quad (6)$$

For large r_1 the right-hand side vanishes, and F_n satisfies the wave equation

$$\left\{\nabla^2 + \frac{8\pi^2 m}{h^2}(E - E_n)\right\}F_n = 0, \quad (7)$$

which is the wave equation for a free particle of energy $E - E_n$. The associated wave-length is $2\pi/k_n$, where

$$k_n^2 = 8\pi^2 m(E - E_n)/h^2. \quad (8)$$

We notice that this wave-length is only real if $E > E_n$, i.e. if the electron has enough energy to excite the nth state of the atom. In this section we consider values of n for which this is the case.

Since the conditions of the problem require the electron to be incident on an atom in its normal state, the function $F_0(\mathbf{r}_1)$ must represent the sum of an incident and scattered wave; thus, F_0 must have the asymptotic form

$$F_0 \sim e^{ik_0 z} + r^{-1}e^{ik_0 r}f_0(\theta, \phi). \quad (9)$$

The functions F_n must represent scattered waves only, and so have asymptotic form

$$F_n \sim r^{-1}e^{ik_n r}f_n(\theta, \phi). \quad (10)$$

From (10) we deduce that $r^{-2}|f_n(\theta, \phi)|^2$ is the number of electrons per unit volume at distance r from the atom, which have excited the state n. Of these, the number crossing unit area per unit time is proportional to $k_n r^{-2}|f_n|^2$, whereas in the incident beam the number crossing unit area per unit time is proportional to k_0. Hence we have (cf. Chap. II, § 1)

$$I_n(\theta)\,d\omega = \frac{k_n}{k_0}|f_n(\theta, \phi)|^2\,d\omega. \quad (11)$$

The calculation of the asymptotic form of the functions $F_n(\mathbf{r}_1)$ cannot be carried out exactly. For high velocities of impact, however, we may readily obtain approximate formulae by a method due to Born.† Under these circumstances the perturbation of the incident

† *Zeits. f. Physik*, **37** (1926), 863, and **38** (1926), 803.

wave by its interaction with the atom will be small.† We take, then, as zero order approximation for Ψ, simply

$$\Psi = \exp(ik_0\mathbf{n}_0\cdot\mathbf{r}_1)\psi_0(\mathbf{r}_2). \tag{12}$$

Here $\exp(ik_0\mathbf{n}_0\cdot\mathbf{r}_1)$ is the plane wave, representing the motion of the incident electron in the direction of the unit vector $\mathbf{n}_0$, when there is no interaction with the atom. Substituting (12) on the right-hand side of (6), we obtain

$$(\nabla^2+k_n^2)F_n(\mathbf{r}_1) = \frac{8\pi^2 m}{h^2}\int\left(\frac{\epsilon^2}{r_{12}}-\frac{\epsilon^2}{r_2}\right)\exp(ik_0\mathbf{n}_0\cdot\mathbf{r}_1)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\,d\tau_2. \tag{13}$$

The solution of this equation with the correct asymptotic form (10) may be obtained by the method of Chap. VI, § 4, the solution being

$$F_n(\mathbf{r}) =$$
$$\frac{2\pi m}{h^2}\int\int\frac{\exp(ik_n|\mathbf{r}-\mathbf{r}_1|)}{|\mathbf{r}-\mathbf{r}_1|}\exp(ik_0\mathbf{n}_0\cdot\mathbf{r}_1)\left(\frac{\epsilon^2}{r_1}-\frac{\epsilon^2}{r_{12}}\right)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\,d\tau_1\,d\tau_2. \tag{14}$$

The asymptotic form of this solution is‡

$$F_n(\mathbf{r}) \sim$$
$$\frac{2\pi m}{h^2}\cdot r^{-1}e^{ik_n r}\int\int\exp\{i(k_0\mathbf{n}_0-k_n\mathbf{n})\cdot\mathbf{r}_1\}\left(\frac{\epsilon^2}{r_1}-\frac{\epsilon^2}{r_{12}}\right)\psi_0(\mathbf{r}_2)\psi^*(\mathbf{r}_2)\,d\tau_1\,d\tau_2, \tag{15}$$

where $\mathbf{n}$ is a unit vector in the direction of the vector $\mathbf{r}$. Hence

$$I_n(\theta) =$$
$$\frac{4\pi^2 m^2}{h^4}\left|\int\int\exp\{i(k_0\mathbf{n}_0-k_n\mathbf{n})\cdot\mathbf{r}_1\}\left(\frac{\epsilon^2}{r_1}-\frac{\epsilon^2}{r_{12}}\right)\psi_0(\mathbf{r}_2)\psi^*(\mathbf{r}_2)\,d\tau_1\,d\tau_2\right. \tag{16}$$

It is possible to proceed further by this method of approximation, by substituting the expressions (14) for F_n in the function Ψ on the right-hand side of (6) and integrating the equations a second time, and so on. However, this method is very tedious§ in practice and it is better to start from more accurate initial approximations for Ψ in (6); these will be discussed later in § 3.

2. Two-body Collisions in General

These results may be generalized to apply to the collision between any two atoms or molecules or ions. The motion of the system may be described in terms of that of the centre of mass of the complete system, the relative motion of the centres of mass of the two bodies, and the motion of the individual particles of each body relative to the centre of mass of each. Of these the motion of the centre of mass of the complete system is irrelevant and may be separated out. The resulting

equation may be compared with (2) above. The Hamiltonian equation (2) is compounded of three parts, namely,

(A) $\left\{\dfrac{h^2}{8\pi^2 m}\nabla_1^2 + \tfrac{1}{2}mv^2\right\}F = 0,$

representing the unperturbed motion of the incident particle;

(B) $\left\{\dfrac{h^2}{8\pi^2 m}\nabla_2^2 + \left(E_0 + \dfrac{\epsilon^2}{r_2}\right)\right\}\psi = 0,$

representing the internal motion of the atomic electron; and

(C) *minus* the interaction energy, $\epsilon^2/r_1 - \epsilon^2/r_{12}$.

Let us now see what terms must replace these in the general case. For the relative motion we have

$$\left\{\frac{h^2}{8\pi^2 M}\nabla^2 + \tfrac{1}{2}Mv^2\right\}F(\mathbf{r}) = 0, \qquad (17)$$

where $\mathbf{r}$ denotes the relative coordinates and M is the reduced mass of the system, i.e. if M_1, M_2 are the masses of the two bodies,

$$M = M_1 M_2/(M_1 + M_2).$$

For the internal motion we have

$$\{H_a(\mathbf{r}_a) - E_a\}u(\mathbf{r}_a) = 0$$

and
$$\{H_b(\mathbf{r}_b) - E_b\}v(\mathbf{r}_b) = 0, \qquad (18)$$

where H_a, H_b are the Hamiltonians of the unperturbed atoms. Corresponding to these equations there will be sets of proper values and proper functions

$$u_n(\mathbf{r}_a), \qquad v_m(\mathbf{r}_b),$$
$$E_a^n, \qquad E_b^m.$$

For convenience of notation we shall not distinguish the two sets of functions, but shall denote each pair of states of the two systems by a single suffix n. The wave function $\psi_n(\mathbf{r}_a, \mathbf{r}_b)$ of the two systems will then be the product of two functions, $u_n(\mathbf{r}_a)$, $v_m(\mathbf{r}_b)$, and the corresponding energy value E_n will be the sum $E_a^n + E_b^m$. ψ_n will satisfy the equation

$$\{H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) - E_a - E_b\}\psi = 0. \qquad (19)$$

Finally, we have an interaction term $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$. The complete wave equation is now

$$\left[\frac{h^2}{8\pi^2 M}\nabla_r^2 - H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) + \tfrac{1}{2}Mv^2 + E_0 - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)\right]\Psi = 0, \qquad (20)$$

and it is easily found by the method of § 1 that the differential cross-section (in relative coordinates) for the transition from state n to state m of the combined system will be given, within the range of validity

of Born's first approximation, by

$$I_{n,m}(\theta) = \frac{4\pi^2 M^2}{h^4}\Big|\int\int\int V(\mathbf{r},\mathbf{r}_a,\mathbf{r}_b)\exp\{i(k_n\mathbf{n}_0-k_m\mathbf{n})\cdot\mathbf{r}\}\psi_m^*\psi_n\,d\tau_a\,d\tau_b\,d\tau\Big|^-,$$

(21)

where

$$k_n = 2\pi M v/h,$$

$$k_m^2 = \frac{8\pi^2 M}{h^2}[\tfrac{1}{2}Mv^2 + E_n - E_m],$$

(22)

and v is the initial relative velocity of the colliding systems. To obtain this differential cross-section in the coordinate system in which one of the bodies is initially at rest, it is only necessary to apply the classical laws of conservation of momentum and energy. The resulting formulae are given in § 5 of this chapter.

In the same way we may readily generalize all the formulae of § 1.

3. Approximate Methods for Slow Collisions

The first approximation in Born's method is only valid when the energy of relative motion in the collision is great compared with the energy of the internal motions involved. For an important class of collisions this condition is not satisfied, and it is necessary to develop methods of practical value for such cases. We will describe two methods, the method of distorted waves and the method of perturbed stationary state functions.†

3.1. *The Method of Distorted Waves.*

Generalizing formula (6) of § 1, we see that the functions $F_n(\mathbf{r})$ satisfy the series of equations

$$[\nabla^2 + k_n^2]F_n(\mathbf{r}) = \frac{8\pi^2 M}{h^2}\int\int V(\mathbf{r},\mathbf{r}_a,\mathbf{r}_b)\Psi\psi_n^*\,d\tau_a\,d\tau_b \qquad (n = 0, 1, 2,...).$$

(23)

Writing

$$\Psi = \sum F_m(\mathbf{r})\psi_m(\mathbf{r}_a,\mathbf{r}_b),$$

and

$$V_{nm}(\mathbf{r}) = \int V(\mathbf{r},\mathbf{r}_a,\mathbf{r}_b)\psi_n\psi_m^*\,d\tau_a\,d\tau_b,$$

(24)

we have

$$(\nabla^2 + k_n^2)F_n(\mathbf{r}) = \frac{8\pi^2 M}{h^2}\sum F_m V_{mn}.$$

(25)

Born's approximation is obtained by taking on the right-hand side of (25)

$$F_0 = \exp(ik_0\mathbf{n}_0\cdot\mathbf{r}); \qquad F_m = 0 \quad (m \neq 0).$$

We make now the less drastic assumption that the non-diagonal matrix elements V_{nm} are so small that we may neglect all products on the right-hand side except $V_{nn}F_n$ and $V_{0n}F_0$, which involves the incident

† An extension of the method of distorted waves is described in Chap. XIII, § 3.3.

wave. We obtain thus the series of equations

$$\left[\nabla^2 + k_0^2 - \frac{8\pi^2 M}{\hbar^2}V_{00}\right]F_0(\mathbf{r}) = 0, \tag{26.1}$$

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2}V_{nn}\right]F_n(\mathbf{r}) = \frac{8\pi^2 M}{\hbar^2}V_{0n}(\mathbf{r})F_0(\mathbf{r}) \qquad (n \neq 0). \tag{26.2}$$

If $V_{00}(\mathbf{r})$, $V_{nn}(\mathbf{r})$ are spherically symmetrical, one may obtain a formal solution of these equations, satisfying the boundary conditions (9), (10), by the methods of Chapters II and VI. In Chap. II, eq. (16), a solution of equation (26.1) was obtained satisfying the boundary condition (9), i.e. having the asymptotic form

$$e^{ik_0 z} + f(\theta)r^{-1}e^{ik_0 r}. \tag{27}$$

We denote this solution by $F_0(\mathbf{r})$.

If we substitute this form for $F_0(\mathbf{r})$ in the right-hand side of (26.2), we obtain an inhomogeneous equation for $F_n(\mathbf{r})$ of the form

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2}V_{nn}(r)\right]F_n = s_n(r, \theta, \phi). \tag{28}$$

The problem of obtaining solutions of this equation with the asymptotic form (10) has been solved in Chap. VI, § 3. If we denote by $\mathfrak{F}_n(r, \theta)$ the solution of the homogeneous equation

$$\left[\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2}V_{nn}(r)\right]\mathfrak{F} = 0 \tag{29}$$

which has the asymptotic form

$$\mathfrak{F}_n(r, \theta) \sim e^{ik_n z} + r^{-1}e^{ik_n r} \times \text{function of } \theta,$$

the asymptotic form of the required solution of (26.2) is

$$F_n(\mathbf{r}) \sim -r^{-1}e^{ik_n r}\frac{2\pi M}{\hbar^2}\int V_{0n}(\mathbf{r}')F_0(r', \theta')\mathfrak{F}_n(r', \pi-\Theta)\,d\tau', \tag{30}$$

where

$$\cos\Theta = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi-\phi'), \tag{31}$$

θ being the angle of scattering. Referring to (10) and (11), we see that the differential cross-section corresponding to excitation of the nth state is now given in relative coordinates by

$$I_n(\theta) = \frac{k_n}{k_0}\frac{4\pi^2 M^2}{\hbar^4}\left|\int\int\int V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)\psi_0\psi_n^* F_0(r', \theta')\mathfrak{F}_n(r', \pi-\Theta)\,d\tau_a\,d\tau_b\,d\tau\right|^2. \tag{32}$$

This formula reduces to Born's expression (21) if we take the functions F_0, $\mathfrak{F}_n$ to be plane waves. We see then that this method takes into

account the distortion of the incident and outgoing waves by the scattering field. The function $F_0(r, \theta)$ represents the motion of the electron in the field $V_{00}(r)$ of the initial state, $\mathfrak{F}_n(r', \pi - \Theta)$ that in the field $V_{nn}(r)$ of the excited state.

Formula (32) is applied in Chap. XI, § 5, to the scattering of electrons by atoms, in Chap. XIII, § 3.2, to the transfer of excitation, and in Chap. XIII, § 3.5, to the excitation of nuclear vibration and rotation in molecular collision. It has also been applied by Gamow† to the collisions of α-particles with atomic nuclei.

3.2. The Case of Exact Resonance.

The validity of the previous method of approximation depends on the smallness of the non-diagonal matrix-elements of the interaction energy. In considering the excitation of the nth stationary state by the impact it is thus only necessary to include the interaction of two waves, the incident and elastically scattered, and that scattered after excitation of the nth state. Further, the effect of the reaction of the inelastic on the elastic scattering need not be taken into account. We may therefore regard the method as one of successive approximations to the solution of the simultaneous equations

$$[\nabla^2 + k_0^2 - (8\pi^2 M/h^2)V_{00}]F_0 = (8\pi^2 M/h^2)V_{0n}F_n,$$
$$[\nabla^2 + k_n^2 - (8\pi^2 M/h^2)V_{nn}]F_n = (8\pi^2 M/h^2)V_{0n}F_0 \tag{33}$$

on the assumption that the matrix-element V_{0n} is small. Now in certain other cases it is sufficient to consider the interaction of two states only, but the matrix-element $V_{0n}(\mathbf{r})$ associated with these states may not be small. Such cases occur when the states 0, n are nearly in resonance, i.e. the energy difference ΔE between the states is small compared with that between any other pair of states. We then obtain as before the simultaneous equations (33), but the method of successive approximations is not in general applicable. It is then more difficult to obtain a satisfactory method of treatment.

In the special case of exact resonance between the two states (as, for example, in considering electron transfer from a helium atom to a helium positive ion) we may obtain an exact solution, but for other cases more complicated methods due to London and to Stueckelberg must be used. These methods will be discussed in Chapter XIII. We will now consider the special case of exact resonance.

Writing $k_0^2 = k_n^2 = k^2$ in (33), and assuming that the field V_{nn} is the

† *Atomic Nuclei and Radioactivity*, Oxford University Press, Chap. IV. See also Massey, *Proc. Roy. Soc. A*, **137** (1932), 447.

same as V_{00}, we obtain the equations

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2}V_{00}(r)\right]F_0(\mathbf{r}) = \frac{8\pi^2 M}{h^2}V_{0n}(\mathbf{r})F_n(\mathbf{r}), \qquad (34.1)$$

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2}V_{00}(r)\right]F_n(\mathbf{r}) = \frac{8\pi^2 M}{h^2}V_{0n}(\mathbf{r})F_0(\mathbf{r}). \qquad (34.2)$$

These equations must be solved subject to the boundary conditions
that for large r

$$F_0(\mathbf{r}) \sim e^{ikz} + r^{-1}e^{ikr}f_0(\theta, \phi),$$
$$F_n(\mathbf{r}) \sim \quad\ r^{-1}e^{ikr}f_n(\theta, \phi). \qquad (35)$$

By addition and subtraction of (34.1), (34.2) we obtain the independent
equations

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2}\{V_{00} + V_{0n}\}\right]\{F_0 + F_n\} = 0 \qquad (36.1)$$

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 M}{h^2}\{V_{00} - V_{0n}\}\right]\{F_0 - F_n\} = 0. \qquad (36.2)$$

If the functions V_{00}, V_{0n} are spherically symmetrical, we may solve
these equations by the method of Chapter II. We obtain (Chap. II,
eq. (17)) solutions of asymptotic form

$$F_0 + F_n \sim \frac{1}{2}\left[e^{ikz} + e^{ikr}\frac{1}{2ikr}\sum_s(2s+1)(e^{2i\eta_s}-1)P_s(\cos\theta)\right], \quad (37.1)$$

$$F_0 - F_n \sim \frac{1}{2}\left[e^{ikz} + e^{ikr}\frac{1}{2ikr}\sum_s(2s+1)(e^{2i\delta_s}-1)P_s(\cos\theta)\right]. \quad (37.2)$$

For definitions of the phases η_s, δ_s, cf. Chap. II, § 1. Solving (37) for F_n,
we obtain

$$F_n \sim r^{-1}e^{ikr}\frac{1}{4ik}\sum_s(2s+1)(e^{2i\eta_s}-e^{2i\delta_s})P_s(\cos\theta). \qquad (38)$$

The differential cross-section corresponding to transfer of excitation
will then be

$$I_n(\theta)\,d\omega = \frac{1}{16k^2}\sum(e^{2i\eta_s}-e^{2i\delta_s})(2s+1)P_s(\cos\theta)\ d\omega, \qquad (39)$$

and the total cross-section

$$Q_n = \frac{\pi}{k^2}\sum_s(2s+1)\sin^2(\eta_s-\delta_s). \qquad (40)$$

Comparison with the corresponding formulae of Chapter II (eqs.
(17) and (18)) shows the similarity of this method to the method of
partial cross-sections applied there to the scattering by a static field
of force.

We are now in a position to examine the condition of validity of the

method of distorted waves described above in § 3.1. Applying this method to the problem discussed in this section, we obtain, since $V_{00} = V_{nn}$, the formula

$$Q_n = \frac{8\pi^3 M^2}{h^4} \int^{\pi} \left| \int V_{0n}(r') F_0(r', \theta') \mathfrak{F}_0(r', \pi-\Theta) \, d\tau' \right|^2 \sin \theta \, d\theta. \qquad (41)$$
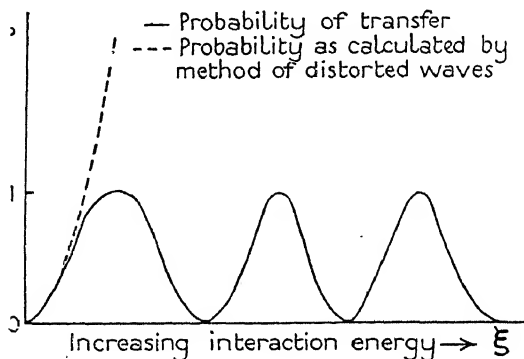

— Probability of transfer
--- Probability as calculated by
    method of distorted waves

Increasing interaction energy → ξ

Fig. 11

Using the expansions

$$F_0(r, \theta) = \frac{1}{k} \sum_s (2s+1) i^s e^{i\gamma_s} F_0^s(r) P_s(\cos \theta)$$

$$\mathfrak{F}_0(r, \pi-\Theta) = \frac{1}{k} \sum (2s+1) i^{-s} e^{i\gamma_s} F_0^s(r) P_s(\cos \Theta), \qquad (42)$$

we obtain

$$Q_n = \frac{\pi}{k^2} \sum_s (2s+1) \left\{ \frac{16\pi^2 M}{kh^2} \int V_{0n} \{F_0^s(r)\}^2 r^2 \, dr \right\}^2. \qquad (43)$$

To prove the validity of the method of distorted waves we must demonstrate the approximate equality of the expressions

$$\sin(\eta_s - \delta_s), \qquad \frac{16\pi^2 M}{kh^2} \int V_{0n} \{F_0^s(r)\}^2 r^2 \, dr. \qquad (44)$$

Provided both quantities are small, this may be shown by the method of Chap. II, § 2. Thus the condition of validity of the method of distorted waves is that the second expression in (44) should be small compared with unity. The range of validity of the distorted wave method of approximation for the calculation of the probability of transfer of excitation is illustrated in general terms in Fig. 11, which also shows the manner in which the approximate method becomes inaccurate.

VIII, § 3 METHODS FOR SLOW COLLISIONS In this figure the probability P of energy transfer is represented as a function of a parameter ξ which is taken to indicate the effective magnitude of V_{0n}. The relative velocity of the impacts is considered fixed. As ξ increases, the probability of transfer will increase from zero towards a value unity. After this value is attained the probability will oscillate as shown. The distorted wave method of approximation is valid only in the region of the initial increase of probability from zero. It predicts a monotonic increase of probability with ξ, and we must expect it always to indicate too great a probability of the transfer process. Similar behaviour will be manifest in the behaviour of the probability as a function of relative velocity of impact, for a fixed value of the parameter ξ. Thus at low velocities the distorted wave method will give too large a probability.†

These general considerations indicate that when results of not too great an accuracy are required we may use the integrals (44) to represent the phases $\eta_s - \delta_s$ in formula (40). In this way the approximate method will never give a probability greater than unity, and in cases where the main contribution to the cross-section arises from terms Q_n such that $|\eta_s - \delta_s| \leqslant \frac{1}{2}\pi$ (which is usually so in practice) a very good approximation will be obtained.

So far we have considered only the case of exact resonance. When the resonance is no longer exact it is impossible to obtain an exact solution of the simultaneous equations (33). It is therefore important to determine the conditions under which the approximate method of § 3.1 is applicable. By a generalization of the results obtained above for the case of exact resonance, we see that the approximate solution obtained by the method of § 3.1 is valid if

$$\frac{16\pi^2 M}{(kk_n)^{\frac{1}{2}}h^2} \int V_{0n} F_0^s F_n^s r^2 \, dr \ll 1 \tag{45}$$

for all s.

When this condition is not satisfied, it is necessary to use some different method of approximation (cf. Chap. XIII, § 3.32).

3.3. *Method of Perturbed Stationary State Wave Functions.*

In calculating the probability of excitation of a given state by the previous methods, we have neglected altogether the interaction of all the states except the initial state and the state under consideration. This neglect may often be serious, and no method of taking this into account in a completely satisfactory manner has yet been developed.

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† Cf. Chap. XI, §§ 3.2, 3.3, 5.2; Chap. XIII, § 3.3.

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However, an approximate method of doing so will now be described. In this we start from stationary state wave functions which are already perturbed by the interaction of the colliding particle, treated as though it were at rest. We restrict ourselves in this section to the case where both systems are spherically symmetrical.

As before, we have to solve the equation

$$\left[\frac{h^2}{8\pi^2 M}\nabla_r^2 - H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) + E\right]\Psi = 0, \qquad (46)$$

with the usual boundary conditions. We first consider the equation

$$[H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) + V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) - E(r)]\chi = 0 \qquad (47)$$

in which $\mathbf{r}$, the relative coordinates of the two systems, appear as parameters. We assume that a solution may be obtained for any value of $\mathbf{r}$, leading to a set of proper functions $\chi_n(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$ and proper values $\epsilon_n(r)$. These functions are classified by their behaviour for large r. We distinguish by the suffix n that energy value which tends, as $r \to \infty$, to E_n, the nth proper value of the equation

$$[H_a(\mathbf{r}_a) + H_b(\mathbf{r}_b) - E]\Psi = 0. \qquad (48)$$

The energy $\epsilon_n(r)$ may then be written

$$\epsilon_n(r) = E_n - \eta_n(r), \qquad (49)$$

where $\eta_n \to 0$ as $r \to \infty$. The functions χ_n form an orthogonal normal set with respect to the coordinates $\mathbf{r}_a$, $\mathbf{r}_b$ for all values of the parameter $\mathbf{r}$. It is therefore possible to expand Ψ in the form

$$\Psi = \sum_n \chi_n(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)F_n(\mathbf{r}), \qquad (50)$$

and, as before, we require solutions for the functions $F_n(\mathbf{r})$ which have the asymptotic form (10), representing outgoing waves.

On substitution in (46), remembering that

$$[-H_a(\mathbf{r}_a) - H_b(\mathbf{r}_b) - V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)]\chi_n = [\eta_n(r) - E_n]\chi_n, \qquad (51)$$

we obtain

$$\sum_n \frac{h^2}{8\pi^2 M}[F_n \nabla_r^2 \chi_n + 2\,\mathrm{grad}_r F_n \cdot \mathrm{grad}_r \chi_n + \chi_n \nabla_r^2 F_n]$$
$$= \sum_n [E_n - \eta_n(r) - E]\chi_n F_n. \qquad (52)$$

We now multiply both sides of this equation by χ_n^* and integrate over the coordinate space of $\mathbf{r}_a$ and $\mathbf{r}_b$. Using the relation

$$\iint \chi_n^* \mathrm{grad}_r \chi_n \, d\tau_a \, d\tau_b = 0,$$

we obtain

$$\frac{h^2}{8\pi^2 M}\nabla^2 F_n + [E-E_n+\eta_n(r)]F_n = -\sum_m{}' F_m(r)\frac{h^2}{8\pi^2 M}\int\int \chi_n^* \nabla_r^2 \chi_m\, d\tau_a\, d\tau_b -$$

$$-2\sum_{m\neq n}\frac{h^2}{8\pi^2 M}\operatorname{grad} F_m(\mathbf{r})\cdot\int\int \chi_n^*\operatorname{grad}_r \chi_m\, d\tau_a\, d\tau_b. \quad (53)$$

These equations replace equations (23), which were obtained by expanding in a series of unperturbed stationary state wave functions. To obtain approximate solutions we use methods exactly similar to those used in § 3.1.

Neglecting non-diagonal matrix-elements, except those referring to the initial state, we obtain

$$\nabla^2 F_0 + \left[\frac{8\pi^2 M}{h^2}\{E-E_0+\eta_0(r)\}+\int\int \chi_0^* \nabla_r^2 \chi_0\, d\tau_a\, d\tau_b\right]F_0 = 0,$$

$$\nabla^2 F_n + \left[\frac{8\pi^2 M}{h^2}\{E-E_n+\eta_n(r)\}+\int\int \chi_n^* \nabla_r^2 \chi_n\, d\tau_a\, d\tau_b\right]F_n$$

$$= -F_0\int\int \chi_n^* \nabla_r^2 \chi_0\, d\tau_a\, d\tau_b - 2\operatorname{grad}F_0\cdot\int\int \chi_n^*\operatorname{grad}_r \chi_0\, d\tau_a\, d\tau_b. \quad (54)$$

These inhomogeneous equations may be solved in the same way as the equations (26.1), (26.2).

In order to compare these equations with those obtained by the method of expansion in unperturbed stationary state wave functions, we will use as the functions χ_n those obtained from (51) by a first-order perturbation calculation, treating V as small. To this approximation we obtain by the usual method†

$$\chi_n = \psi_n + \sum_{m\neq n}{}' V_{mn}\psi_m/(E_n-E_m),$$

$$= -\eta_n + V_{nn} + \sum_{m\neq n}{}'\frac{V_{nm}V_{mn}}{E_n-E_m},$$

where $V_{nm} = \int\int V(\mathbf{r},\mathbf{r}_a,\mathbf{r}_b)\psi_m^*(\mathbf{r}_a,\mathbf{r}_b)\psi_n(\mathbf{r}_a,\mathbf{r}_b)\, d\tau_a\, d\tau_b.$

We thus obtain from (54)

$$\nabla^2 F_n +$$

$$+\left[\frac{8\pi^2 M}{h^2}\{E-E_n-V_{nn}(r)\}+\sum_{m\neq n}\frac{V_{mn}}{(E_m-E_n)^2}\left\{\nabla_r^2+\frac{8\pi^2 M}{h^2}(E_m-E_n)\right\}V_{nm}\right]F_n$$

$$= -F_0\left[\frac{\nabla^2 V_{0n}}{E_0-E_n}-\sum_{m\neq n,0}\frac{V_{mn}\nabla_r^2 V_{0m}}{(E_n-E_m)(E_m-E_0)}\right]-$$

$$2\operatorname{grad}_r F_0\cdot\left[\frac{\operatorname{grad}_r V_{0n}}{E_0-E_n}-\sum_{m\neq n}\frac{V_{mn}\operatorname{grad}_r V_{0m}}{(E_n-E_m)(E_m-E_0)}\right]. \quad (55)$$

† Cf. Sommerfeld, *Wave Mechanics*, p. 144.

If we neglect on the right-hand side of (55) matrix elements involving states other than 0 and n, we obtain the equation

$$\nabla^2 F_n + \frac{8\pi^2 M}{h^2}\{E - E_n - V_{nn}(r)\}F_n$$

$$= -F_0\,\nabla^2 V_{0n}/(E_n - E_0) - 2\,\mathrm{grad}\,F_0 \cdot \mathrm{grad}\,V_{0n}/(E_n - E_0).$$

Solving this equation by the same method as that used in § 3.1 and using the differential equation for F_0, we obtain, for the differential cross-section corresponding to the excitation, the formula

$$I_n(\theta)\,d\omega$$

$$= \frac{k_n}{k_0}\frac{4\pi^2 M^2}{h^4}\left| \int \left(1 - \frac{8\pi^2 M}{h^2}\frac{V_{00} - V_{nn}}{k^2 - k_n^2}\right)V_{0n}(\mathbf{r'})F_0(r',\theta')\mathfrak{F}_n(r',\pi - \Theta')\,d\tau' \right|^2.$$

We see that, apart from the term $(V_{00} - V_{nn})/(k^2 - k_n^2)$, this formula reduces to that obtained from the method of distorted waves. Exact equivalence of the two formulae would not be expected owing to the different initial assumptions. Provided $V(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b)$ is small the formula reduces to Born's approximation for high velocities of impact, but this is not so when the interaction is large. Under the latter conditions the method described in this section is only valid when the relative velocity of the impact is small compared with that of the internal motions concerned.

However, if it is possible to obtain the perturbed stationary state wave functions with a reasonable degree of accuracy, the calculation of the scattered amplitudes by the method of this section should lead to results of greater accuracy than the previous methods, the interaction of the higher states being automatically included to some extent in the initial approximations. Owing, however, to the comparative difficulty of obtaining accurate perturbed functions, the method has as yet had only limited application.† We discuss the method here, because we believe that it offers the chief hope of a future improvement in the technique of these problems. A somewhat similar method has, however, been applied by London in discussing the simultaneous equations (33) of § 3.2, but in this only two states are considered throughout. This is permissible if two states are in approximate resonance, and London applied the method to obtain approximate solutions of the simultaneous equations (33) in a form valid when the interaction term V_{0n} is large. London's method will be considered further in Chap. XIII, § 3.32.

† See, however, Chap. XIII, § 3.4.

3.4. *Summary of Methods.*

Before proceeding to the consideration of rearrangement collisions we will summarize the methods available for the calculation of the probabilities of inelastic collisions under various conditions. A convenient way of doing this is by means of the following table.

<div align="center">TABLE I</div>

Conditions defining Collision.

Relative Velocity.	Magnitude of Matrix Elements of the Interaction Energy.		Method available.	Examples.
	Diagonal elements (V_{nn}).	Non-diagonal elements (V_{0n}).		
Great compared with that of internal motions.	any magnitude	any magnitude	Born's approximation	Scattering of fast electrons or α-particles.
Less than or comparable with that of internal motions.	small	small	Born's approximation.	
,, ,,	large	small	Method of distorted waves.	Excitation of molecular vibration by impact of atoms.
,, ,,	any magnitude	All small except V_{0n} where 0th and nth state are in approximate resonance.	Solution of simultaneous equations (33) (e.g. by London's method).	Transfer of electronic excitation.
,, ,,	any magnitude.	All comparable and not small.	Method of perturbed stationary state wave functions.	Excitation and ionization by slow positive ions.

4. Rearrangement Collisions

4.1. *Electron Exchange.*

As an example of the type of phenomenon to be considered under this heading, we return to the problem of § 1, namely, the collision between an electron and a hydrogen atom. We obtained in § 1 the probability that the incident electron should be scattered into a given solid angle after exciting the nth state. It is also possible that the incident electron may be captured into the nth state, and the atomic electron ejected. We refer to this phenomenon as electron exchange, and must now calculate its probability.

In order to calculate the probability of direct scattering, in § 1 we expanded the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ describing the collision in the form

$$\Psi = \left(\sum_n + \int\right) F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2), \tag{56}$$

where F_0 represents an incident wave and a scattered wave, and F_n a scattered wave, so long as the excitation energy of the state n is smaller than the energy of the incident electron. When this is no longer the case, F_n falls off exponentially; the values of n in (56) which correspond to the continuous spectrum thus give us the possibility that the incident electron is captured and the atomic electron ejected. To obtain the probability of this event, we expand (56) in the alternative form

$$\Psi = \left(\sum_n + \int\right) G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1). \tag{57}$$

Assuming† that G_n has asymptotic form

$$G_n \sim r^{-1}e^{ik_n r}g_n(\theta, \phi), \tag{58}$$

the probability that the incident electron is captured into the nth state, and the atomic electron ejected into the solid angle $d\omega$, is

$$\frac{k_n}{k_0}|g_n(\theta, \phi)|^2\, d\omega. \tag{59}$$

We must state here that we may only treat the electrons as distinguishable in this way if the spins are antiparallel. For the scattering formulae with unpolarized beams, cf. § 4.3.

We must now show how to calculate g_n. The wave equation is

$$\left\{\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) + E + \frac{\epsilon^2}{r_1} + \frac{\epsilon^2}{r_2} - \frac{\epsilon^2}{r_{12}}\right\}\Psi = 0. \tag{60}$$

It was shown in § 1 that F_n satisfies

$$(\nabla^2 + k_n^2)F_n = \frac{8\pi^2 m}{h^2}\int\left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_1}\right)\Psi\psi_n^*(\mathbf{r}_2)\, d\tau_2. \tag{61}$$

In the same way, substituting (58) into (60), multiplying by $\psi_n^*(\mathbf{r}_1)$, and integrating over all x_1, y_1, z_1, we obtain

$$(\nabla^2 + k_n^2)G_n(\mathbf{r}_2) = \frac{8\pi^2 m}{h^2}\int\left(\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2}\right)\Psi(\mathbf{r}_1, \mathbf{r}_2)\psi_n^*(\mathbf{r}_1)\, d\tau_1. \tag{62}$$

This equation is exact; to solve it, we assume various forms for Ψ on the right-hand side, and obtain a solution of the form (58) by the methods of § 1. It will be noticed that the *approximate* solution thus obtained is not an expansion of the approximate solution of § 1. In

† No proof of this has at present been given, but a proof should be possible.

choosing an approximate Ψ we note that Ψ must satisfy

$$\int \{\Psi - F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)\}\psi_n^*(\mathbf{r}_2)\,d\tau_2 = 0$$

$$\int \{\Psi - G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1)\}\psi_n^*(\mathbf{r}_1)\,d\tau_1 = 0. \qquad (63)$$

If we require results valid only within the accuracy of Born's approximation, we take on the right-hand side of (62) as in § 1

$$\Psi = \exp(ik_0\mathbf{n}_0 \cdot \mathbf{r}_1)\psi_0(\mathbf{r}_2) \qquad (64)$$

and obtain

$$[\nabla^2 + k_n^2]G_n = \frac{8\pi^2 m}{h^2} \int \left\{\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2}\right\}\psi_n^*(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\exp(ik\mathbf{n}_0 \cdot \mathbf{r}_1)\,d\tau_1. \qquad (65)$$

Solving this equation by the method of Chap. VI, § 4, we obtain for the asymptotic form of G_n

$$G_n \sim r^{-1}\exp(ik_n r)g_n(\theta, \phi),$$

where

$$g_n(\theta, \phi) = -\frac{2\pi m}{h^2} \int\int \left\{\frac{\epsilon^2}{r_{12}} - \frac{\epsilon^2}{r_2}\right\}\psi_n^*(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\exp i(k_0\mathbf{n}_0 \cdot \mathbf{r}_1 - k_n\mathbf{n} \cdot \mathbf{r}_2)\,d\tau_1\,d\tau_2$$

$$(66)$$

and $\mathbf{n}$ is a unit vector in the direction θ, ϕ. It is to be noted that the form (64) does not satisfy the equations (63), but for high-velocity impacts when Born's approximation is valid the error made is small. Further discussion of the equation (62) is given in Chap. X, § 8, and Chap. XI, § 5.

4.2. Rearrangement Collisions in General.

Before discussing the effect of the identity of the electrons on the formula for the scattered intensity we shall generalize the method to apply to rearrangement collisions in general. We require the probability that two systems A and B, in the nth and mth states respectively, become rearranged on impact, producing systems C and D in the sth and tth states respectively. In order to follow the method used for the simple case above, we must write the wave equation for the complete system in the form which is most relevant to the discussion of the final systems C and D. Instead of the coordinates which refer to the initial state, we choose now as coordinates the relative coordinates $\boldsymbol{\rho}$ of the centres of mass of the final systems, and the internal coordinates $\mathbf{r}_c$, $\mathbf{r}_d$ of the systems C and D referred to their respective centres of mass. The equation (20) may now be written

$$\left[-\frac{h^2}{8\pi^2 M'}\nabla'^2 + H_c(\mathbf{r}_c) + H_d(\mathbf{r}_d) + V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) - E\right]\Psi = 0, \qquad (67)$$

where M' is the reduced mass, $M_c M_d/(M_c + M_d)$, of the final systems,

H_c, H_d the Hamiltonian operators of the internal motion of the bodies C and D, and $V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho})$ the interaction energy between C and D.

We distinguish a given pair of stationary states of the systems C and D by the suffix s and write the corresponding wave functions and energies as $\phi_s(\mathbf{r}_c, \mathbf{r}_d)$, E_s respectively. $\phi_s(\mathbf{r}_c, \mathbf{r}_d)$ is then the product of two wave functions $u_p(\mathbf{r}_c)$, $v_q(\mathbf{r}_d)$ of the separate systems, and E_s the sum of the corresponding energy values, $E_c^p + E_d^q$. This notation corresponds exactly with that used in § 2.

Comparing the equation (67) with (60), we see that the formulae of § 4.1 may be generalized by writing

$$M' \text{ for } m, \qquad\qquad \psi_0(\mathbf{r}_a, \mathbf{r}_b) \text{ for } \psi_0(\mathbf{r}_1),$$

$$-V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) \text{ for } \epsilon^2\left(\frac{1}{r_2} - \frac{1}{r_{12}}\right), \qquad \phi_s(\mathbf{r}_c, \mathbf{r}_d) \text{ for } \psi_s(\mathbf{r}_2).$$

To the accuracy of Born's first approximation, we obtain then, for the differential cross-section (in the relative coordinates $\boldsymbol{\rho}$) corresponding to the rearrangement in which the sth state of the systems C and D is excited, the formulae

$$I_s(\theta, \phi)\, d\omega = \frac{k_s'}{k} |g_s(\theta, \phi)|^2\, d\omega$$

$$\frac{4\pi^2 M'^2 k_s'}{h^4 k}\left| \int \int \int V(\mathbf{r}_c, \mathbf{r}_d, \boldsymbol{\rho}) \exp\{i(k\mathbf{n}_0 \cdot \mathbf{r} - k_s' \mathbf{n} \cdot \boldsymbol{\rho})\} \times \right.$$

$$\left. \times \psi_0(\mathbf{r}_a, \mathbf{r}_b)\phi_s(\mathbf{r}_c, \mathbf{r}_d)\, d\tau_a\, d\tau_b\, d\boldsymbol{\rho} \right|^2 d\omega, \qquad (68)$$

where $k = 2\pi M v/h$, $k_s' = 2\pi M' v_s/h$, v, v_s being the initial and final relative velocities respectively.

As an example we may take the capture of electrons from atoms by α-particles. In this case $\mathbf{r}$ is the vector distance between the centre of mass of the atom and the α-particle, $\boldsymbol{\rho}$ the distance between the centre of mass of the ionized atom and the centre of mass of the helium ion formed by the capture. For the internal coordinates we have initially the coordinates of the electron relative to the centre of mass of the atom and, finally, the coordinates of the same electron relative to the centre of mass of the helium ion. The application of the formula (68) for this case is discussed in Chap. XIII, § 2.2.

In the case of collisions between atoms or other heavy particles in which electron transfer takes place on impact, it is possible to apply the method of perturbed stationary state wave functions (§ 3.3) without modification. This is possible, because the small mass of the electron

has no appreciable effect on the reduced mass of the atomic systems, so this may be taken as unaltered by the electron transfer.

4.3. *Effect of the Exclusion Principle on the Scattering Formulae.*†

We return in this section to the problem of the scattering of electrons by a hydrogen atom. We limit ourselves to the case when the energy of the incident electron is so low that excitation is impossible. Then the collision is described by a wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ with asymptotic form

$$\Psi \sim [\exp ikz_1 + r_1^{-1}f(\theta_1)\exp ikr_1]\psi(r_2) \qquad (r_1 \text{ large}),$$
$$\sim [r_2^{-1}g(\theta_2)\exp ikr_2]\psi(r_1) \qquad (r_2 \text{ large}).$$

If the electrons were distinguishable one could deduce that the number of electrons scattered was proportional to $|f|^2$, and the number ejected to $|g|^2$. However, as shown in Chapter V, one must use antisymmetrical wave functions. The wave function symmetrical or antisymmetrical in the space coordinates is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \pm \Psi(\mathbf{r}_2, \mathbf{r}_1),$$

which has asymptotic form, for large r_1, say,

$$[e^{ikz_1} + \{f(\theta) \pm g(\theta)\}r_1^{-1}e^{ikr_1}]\psi(r_2).$$

Using either formula, one obtains the result that the number of electrons scattered or knocked into the solid angle $d\omega$ is

$$|f(\theta) \pm g(\theta)|^2 \, d\omega.$$

As shown in Chap. V, § 5, we must combine these formulae in the ratio 1 to 3 for unpolarized electrons. The total number scattered into the solid angle $d\omega$ is thus

$$\{\tfrac{3}{4}|f-g|^2 + \tfrac{1}{4}|f+g|^2\} \, d\omega. \tag{69}$$

Let us now consider the case of electron collisions with helium. We denote the second atomic electron by the suffix 3, so the collision is described by a wave function

$$\Psi \sim \{e^{ikz_1} + f(\theta_1)r_1^{-1}e^{ikr_1}\}\psi(r_2, r_3) \qquad (r_1 \text{ large}),$$
$$\sim g(\theta_2)r_2^{-1}e^{ikr_2}\psi(r_1, r_3) \qquad (r_2 \text{ large}),$$
$$\sim g(\theta_3)r_3^{-1}e^{ikr_3}\psi(r_2, r_1) \qquad (r_3 \text{ large}).$$

By following through an argument very similar to that used above for hydrogen, we find that the total number of electrons scattered into the solid angle $d\omega$ is

$$|f-g|^2 \, d\omega. \tag{70}$$

† Oppenheimer, *Phys. Rev.*, **32** (1928), 361.

5. Collisions between Two Systems, One of which is initially at Rest.

In several sections of this book (Chap. V, § 3; Chap. VIII, §§ 2, 3, 4; Chap. XV, § 3) we have found the differential cross-section, $I(\theta)\,d\omega$, for collisions between two particles in which their centre of gravity is at rest. This is found by solving the equation

$$\nabla^2\psi + (8\pi^2 m/h^2)(\tfrac{1}{2}mv^2 - V)\psi = 0,$$

where m is the 'reduced mass', $m_1 m_2/(m_1+m_2)$, of the two particles, and v their relative velocity. If a solution is found of the form

$$\psi \sim e^{ikz} + r^{-1}e^{ikr}f(\theta),$$

then $I(\theta) = |f(\theta)|^2$. We show in this section how to find the differential cross-section when one particle, m_1, is initially at rest. Denoting by $J(\Theta)\,d\Omega$ the differential cross-section in this case for scattering through an angle Θ into the solid angle $d\Omega$, we have

$$J(\Theta)\sin\Theta = I(\theta)\sin\theta\,d\theta/d\Theta,$$

where $\qquad\qquad \tan\Theta = m_1\sin\theta/(m_1\cos\theta + m_2).$

In the special case where the masses are equal, $\Theta = \tfrac{1}{2}\theta$, and hence (unless the two particles are similar, cf. Chap. V, eq. (26))

$$J(\Theta) = I(2\Theta)\,4\cos\Theta.$$

THE COLLISIONS OF FAST ELECTRONS WITH ATOMS. ELASTIC SCATTERING—BORN'S APPROXIMATION

1. Introductory. The Experimental Methods and Results

In this chapter, and in Chapters X, XI, XII, and XIII, we apply the general theory of Chapter VIII to the detailed investigation of particular problems. Of these the most important are those associated with the collisions of electrons with atoms. The results of the calculations are expressed in terms of the differential and total cross-sections corresponding to collisions in which the nth state of the atom is excited by electrons of definite velocity v. These will be denoted by $I_n(\theta)$ and Q_n respectively,† and are such that

$$2\pi \int_0^\pi I_n(\theta)\sin\theta\, d\theta = Q_n. \tag{1}$$

For the case of the excitation of continuous energy-levels, a level is defined by a quantity κ such that the energy corresponding to the level is given by

$$E_\kappa = \kappa^2 h^2/8\pi^2 m. \tag{2}$$

The cross-section corresponding to excitation of a set of levels between κ and $\kappa+d\kappa$ is then denoted by $Q_\kappa\, d\kappa$.

The differential cross-section determines the angular distribution of the scattered electrons, whereas the total cross-section determines the total probability of excitation of the given state.

As it is of importance to keep the theory in close relation to the practical side of the subject, we will first outline the different types of experimental investigation concerned with the collisions of electrons with atoms, and indicate the relations of the observed quantities to the calculated differential and total cross-sections. The types of experiment may be classified as follows:

1.1. *Experiments in which the Aggregate of Effects due to All Types of Collision, Elastic and Inelastic, are observed.*

The results of these experiments give information only about the Q's, not the differential cross-sections, and do not usually distinguish between the Q's corresponding to different states. The two types of experiment falling under this head are as follows:

(a) *Measurements of the stopping-power of matter for fast electrons.*

† Cf. Chap. II, § 1.

Here the experimental methods consist in the investigation of the ranges of fast particles in different materials. The stopping-power is defined in terms of the loss of kinetic energy of the electron per cm. of path in the material. Denoting the energies of the bound atomic states by E_n, we see that this rate of loss of kinetic energy is given by

$$-\frac{dT}{dx} = N\left\{ \sum_n Q_n(E_n - E_0) + \int_{\kappa=0}^{\kappa_{max}} (E_\kappa - E_0)Q_\kappa \, d\kappa \right\}, \qquad (3)$$

where E_0 is the energy of the normal state of the atom, and E_κ is given by (2). N is the number of atoms per c.c. of the material, and κ_{max} is related by formula (2) to the maximum energy which the electron can give to the atom.

In certain cases the methods used may be applied to obtain information about individual collisions; the calculation of the stopping-power in terms of this summation is, however, of importance, in view of the application of range measurements to determinations of the initial energy of the particle.[†]

(b) *Measurement of total cross-sections.* If a homogeneous beam of electrons is fired through a gas, the beam becomes diffuse, and, if its initial energy is greater than the resonance potential of the gas, it will also become inhomogeneous.

Let J be the intensity of the electron beam. Then, if we regard every electron which is deviated or loses energy on collision as lost from the beam, the loss of intensity $|\delta J|$ in traversing a distance δx in the gas at pressure p may be written in the form

$$\delta J = -Jap \, \delta x,$$

where a depends only on the nature of the gas and the energy of the electron beam. Integrating this equation, we obtain for the intensity in the beam after traversing a distance x cm.,

$$J = J_0 e^{-apx}.$$

By measuring the variation of the beam current with length of path in the gas the quantity a may be measured. This type of experiment was introduced by Ramsauer[‡] and has been applied by him and by various other investigators to the measurement of a for all simple gases and some metallic and other vapours.[§]

[†] See, for example, Blackett and Occhialini, *Proc. Roy. Soc.*, A, **139** (1933), 699.

[‡] *Ann. der Physik*, **64** (1921), 513.

[§] See, for example, the summary by R. Kollath in *Phys. Zeits.* **31** (1931), 985, and § 1 of Chap. X.

From the definition of the cross-section Q it is clear that, if N is the number of atoms per c.c. in the gas at normal temperature and pressure,

$$a = \frac{Np'}{760}\left[\sum_n Q_n + \int_0^{\kappa_{max}} Q_\kappa \, d\kappa\right],$$

where p' is the unit of pressure (actually 1 mm. Hg) in the units (mm. of mercury) adopted in the experimental determinations. If the cross-sections $Q_n, Q_\kappa \, d\kappa$ are measured in units of πa_0^2, where a_0 is the radius of the first Bohr orbit in hydrogen, we have, for this pressure

$$a = 3 \cdot 15\left[\sum_n Q_n + \int_0^{\kappa_{max}} Q_\kappa \, d\kappa\right].$$

The application of this method, unlike that of the stopping-power investigations, is restricted to electrons of slow to medium velocities[†] (0·5 to 400 volts), and it is seen from the above that it gives only the magnitude of the sums of all cross-sections. For electrons with energies below the resonance potential of the gas, however, only the elastic cross-section Q_0 will be effective; and so in this range of energies the method gives results of especial significance.

It is of interest to point out here that the experimental definition of a given above would be meaningless on the classical theory unless the colliding systems had definite boundaries, and the observed values would depend on the actual definition of a collision provided by the dimensions of the receiving slits of the apparatus. This difficulty does not occur on the quantum theory, as the cross-sections Q are definite, provided that the field of force of the scatterer falls off sufficiently rapidly with distance, a condition satisfied by all atomic fields. This point is discussed in Chapter II, end of § 1, and experimental evidence in its favour is described in Chapter X, § 1.

In connexion with this type of experiment we must also mention the method due to Townsend.[‡] The interpretation of the initial observations in this method requires the use of a complicated classical theory of the motion of electrons in gases, and its application is naturally limited to conditions under which the theory holds, viz. at very low velocities of impact (below 5 volts in most gases). Inasmuch as this method gives information as to the form of Q_0 for much lower electron

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[†] Brode, *Phys. Rev.* **39** (1932), 547, has recently measured a for argon for electrons of energy up to 2,500 volts by a modification of the usual method.

[‡] *Phil. Mag.* **42** (1921), 873.

velocities than the method of Ramsauer, the results obtained by its use are of considerable importance.

1.2. *Experiments in which the Different Types of Collision, Elastic and Inelastic, are investigated separately.*

From the results of these investigations information is obtained about the relative magnitudes of the different cross-sections Q_n for a given incident velocity, and about the differential cross-sections $I_n(\theta)$ as functions of angle of scattering, and also about the variation of any one cross-section Q_n with velocity of impact. Absolute magnitudes are not usually measured, but these may be obtained from experiments of the first type.

For convenience of description these methods may be further divided into three classes:

(a) *Electrical methods.* In experiments of this type direct measurements are made of the angular distributions of scattered electrons or of the relative excitation probabilities, by observing the scattered currents. For the case of ionizing impacts, the absolute ionization cross-section $\int_0^{\kappa_{max}} Q_\kappa \, d\kappa$ may be measured by observing the positive ion current produced by a homogeneous beam of electrons fired through a gas at low pressure.

(b) *Optical methods.* In this type of experiment a homogeneous electron beam is fired through a gas or vapour, and the intensity of the light of different wave-lengths emitted by atoms excited by the electron beam is measured. The intensity of light emitted, corresponding to a switch from a state n to a state m of a gas atom, will be proportional to

$$Q_n A_{nm},$$

where A_{nm} is the optical transition probability from state n to state m. The variation in the intensity of the light of a given wave-length with the velocity of the exciting electrons will then give the variation of Q_n with the velocity of impact, as A_{nm} is independent of the method of excitation. If A_{nm} can be calculated, it is also possible to compare the magnitudes of the cross-sections Q_n for different n.

This method has the advantage of being more sensitive than the electrical method; and thus the behaviour of the cross-sections Q_n may be examined for quite high excited states.

We thus see that the experimental material available is sufficiently diverse to provide ample illustration of the theory and to test its validity. Conversely, the theory is in a position to throw light on a

large variety of phenomena of interest and importance to the physicist. Before proceeding to the detailed calculations of differential and total cross-sections we will consider briefly the order of treatment. We consider first elastic collisions, using the simplest formula, the first approximation of Born's theory, Chap. VII, § 1. The range of validity of this formula is examined and the theory then improved (Chapter X) by using the method of Faxén and Holtsmark given in Chapter II. We then introduce further improvements in certain cases, including a consideration of electron exchange. Up to this point the calculations require no mention of inelastic collisions, but in a more accurate theory one cannot discuss elastic collisions without discussing the inelastic at the same time, and the effect of the interaction of the inelastically scattered waves on the elastic is next briefly discussed. This, then, provides a convenient point (Chapter XI) for the detailed discussion of inelastic collisions. Just as for the elastic collisions, we begin with Born's first approximation (which is sufficient for the calculation of the stopping-power of matter for fast particles) and then consider the improvements necessary for slower particles.

2. Elastic Scattering. Born's First Approximation

It was shown in Chap. VII, § 1, that the differential elastic cross-section $I(\theta)$ for an elastic collision of an electron of velocity v with a spherically symmetrical field of force of potential $V(r)$ is given within the range of validity of Born's first approximation by†

$$I(\theta) = \frac{8\pi^2 m}{\ } \int_0^\infty \frac{\sin Kr}{Kr} V(r) r^2 \, dr \qquad (K = 4\pi m v \sin \tfrac{1}{2}\theta / h). \qquad (4)$$

A second formula showing the relation between (4) and the formula for the scattering of X-rays was also obtained.‡ We have now to calculate $I(\theta)$ when $V(r)$ is the field of an atom.

If $\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z)$ is the wave function of the atom (atomic number Z), we have§

$$V(r) = -\epsilon^2 \int \left(\frac{Z}{r} - \sum_{n=1}^{Z} \frac{1}{|\mathbf{r} - \mathbf{r}_n|} \right) |\psi_0(\mathbf{r}_1, ...)|^2 \, d\tau_1 ... d\tau_Z. \qquad (5)$$

As the wave function ψ_0 is only known analytically for a very few atoms, the calculation of $V(r)$ for most atoms depends on the application of numerical methods; we will first consider the cases where ψ_0 is known analytically.

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† Cf. Chap. VII, eq. (12).   ‡ Chap. VII, eq. (18).
§ Cf. Chap. VIII, §§ 1, 2.

3. Scattering by Hydrogen and Helium

For hydrogen we have $\qquad \psi_0 = (\pi/a_0^3)^{\frac{1}{2}} e^{-r/a_0}.$ (6)

For helium we may take with sufficient approximation the wave function obtained by Hylleraas[†] using a variation method, viz.

$$\psi_0 = (\pi Z^3/a_0^3) e^{-Z(r_1+r_2)/a_0} \qquad (Z = 1\cdot 69). \tag{7}$$

Substituting these expressions in (5) and integrating, we find

$$V(r) = -\epsilon^2\left(\frac{1}{r}+\frac{1}{r}\right)e^{-2r/a_0} \qquad \text{for hydrogen,}$$

$$= -2\epsilon^2\left(\frac{1}{r}+\frac{Z}{a_0}\right)e^{-2Zr/a_0} \qquad \text{for helium.} \tag{8}$$

TABLE I

Scattered Intensities for Helium and Hydrogen.

$\dfrac{ka_0}{Z}\sin\frac{1}{2}\theta.$	$\dfrac{\sqrt{\text{Volts}}}{Z}\sin\frac{1}{2}\theta.$	$\{Z^4 I(\theta)/A\}\times 10^{18} \text{ cm.}^2$
0	0	27·6
0·03	0·11	27·3
0·05	0·18	27·2
0·10	0·37	26·7
0·20	0·74	24·3
0·30	1·10	21·3
0·40	1·47	17·7
0·50	1·84	14·3
0·60	2·21	11·1
0·70	2·59	8·62
0·80	2·94	6·61
0·90	3·31	5·08
1·00	3·68	3·87
1·20	3·82	2·30
1·40	4·46	1·48
1·60	5·10	0·921
1·80	6·10	0·590
2·00	7·36	0·397
2·50	9·20	0·168
3·00	11·0	0·083
3·50	12·9	0·046
4·00	14·7	0·027
4·50	16·6	0·017
5·00	18·4	0·011

$\left.\begin{array}{l} Z = 1 \\ A = 1 \end{array}\right\}$ for hydrogen. $\left.\begin{array}{l} Z = 1\cdot 69 \\ A = 4 \end{array}\right\}$ for helium.

[†] *Zeits. f. Physik,* **54** (1929), 347.

Substituting in the expression (4) for $I(\theta)$, we obtain, after an elementary integration,

$$I(\theta) = \frac{64\pi^4 m^2 \epsilon^4 A (2\lambda^2 + K^2)^2}{h^4 (\lambda^2 + K^2)^4}, \tag{9}$$

where for hydrogen $A = 1,$ $\lambda = 2/a_0,$
and for helium $A = 4,$ $\lambda = 3 \cdot 36/a_0.$

By means of this formula the angular distributions of electrons elastically scattered in hydrogen and helium may readily be calculated. In Table I $I(\theta)$ is tabulated as a function of $v \sin \frac{1}{2}\theta$ for these two atoms.
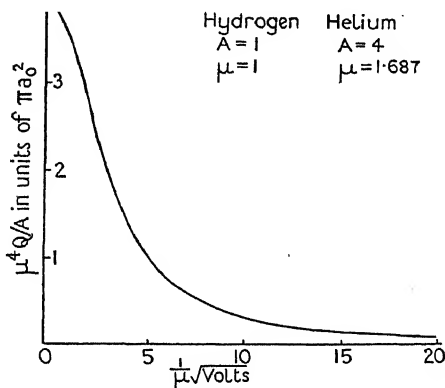
FIG. 12.   Elastic cross-sections for hydrogen and helium.

The total elastic cross-section Q_0 may now be calculated. We have

$$Q_0 = 2\pi \int_0^\pi I(\theta) \sin \theta \, d\theta$$

$$= \frac{1024 A \pi^5 m^2 \epsilon^4 (3\lambda^4 + 18\lambda^2 k^2 + 28k^4)}{3h^4 \lambda^2 (\lambda^2 + 4k^2)^3}. \tag{10}$$

Q_0 is a monotonic function of $k = 2\pi m v/h$, as is clear from Fig. 12, where Q_0 is plotted against k.

3.1. *Comparison with Experiment.*

Measurements of the angular distributions of electrons scattered elastically by helium atoms have been carried out by a number of investigators,† for electrons with energies ranging from $1 \cdot 8$ to 700 volts.

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† Dymond and Watson, *Proc. Roy. Soc.*, A, **122** (1929), 571; McMillen, *Phys. Rev.* **36** (1930), 1034; Bullard and Massey, *Proc. Roy. Soc.*, A, **133** (1931), 637; Ramsauer and

In Fig. 13 the experimental curves for electrons with energies greater than 50 volts are compared with those calculated from the formula (9) above. As the experiments are unable to furnish absolute values of the scattering, the scale has been adjusted so that the observed and calculated values of the scattering for 700-volt electrons agree.
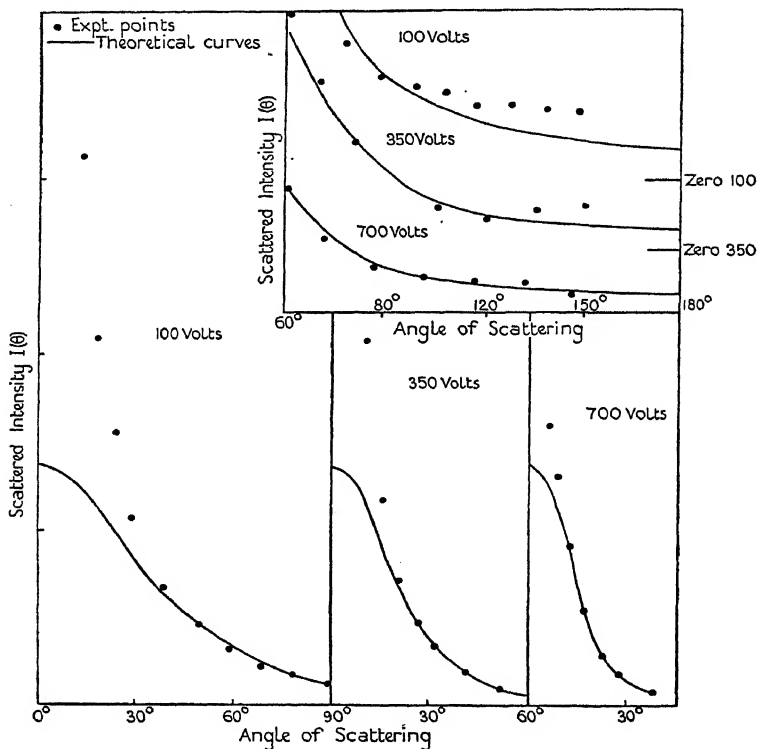
FIG. 13. Angular distributions of electrons scattered by helium atoms.

It is seen that the agreement then obtained at voltages above 100 volts is quite good over a large angular range. However, at both small and large angles of scattering noticeable discrepancies occur. Thus, for electrons with energies less than 500 volts the scattering becomes almost independent of angle at large angles of scattering instead of falling off uniformly with increase of angle (see inset figure). This behaviour is

Kollath, *Ann. der Phys.* **12** (1932), 529; Werner, *Proc. Roy. Soc.*, A, **134** (1932), 202; Hughes, McMillen, and Webb, *Phys. Rev.* **41** (1932), 154; Mohr and Nicoll, *Proc. Roy. Soc.*, A, **138** (1932), 229, 469.

explained in § 5.1 as due to the distortion of the incident wave by the atomic field.

At small angles of scattering the observed variation of intensity with angle is greater than the calculated. This seems to be due to polarization of the atom by the incident electron and will be further discussed in Chap. X, § 10.

For voltages less than 100 volts the agreement is unsatisfactory at all angles. The reasons for these deviations will be discussed in § 5.1 of this chapter and in § 9 of Chapter X.

It thus appears that Born's formula (9) is approximately valid for electrons of energy greater than 100 volts, scattered by helium atoms, but it is not completely accurate over the whole angular range until the electron energy is as great as 500 volts.

Experiments in atomic hydrogen have been carried out by Harnwell,[†] but the observed angular distributions for 180- and 120-volt electrons fall off more steeply with angle than those calculated above. This is not surprising in view of the difficulty of the experiments. For molecular hydrogen there is considerable experimental material available; this will be discussed in Chap. XII, § 3, dealing with the scattering of electrons by molecules.

4. The Calculation of $I(\theta)$ and Q_0 for Complex Atoms

There are two methods available for the determination of the field $V(r)$ for other atoms than H and He: the self-consistent field method of Hartree,[‡] and the statistical method due to Thomas[§] and Fermi[||] in which the atomic electrons are treated as a degenerate gas. Of these two the most accurate is certainly Hartree's method. The application of this method to complicated atoms such as mercury is, however, a lengthy procedure. As a consequence the Hartree fields of atoms with atomic number greater than 37 have not yet been obtained. For the more complex atoms the method of Thomas and Fermi may be applied immediately, and since it is a statistical method it will be more accurate for such atoms than for the lighter ones.

Using potentials given by Hartree's method, the differential cross-sections for collisions of electrons with various atoms may be calculated by numerical integration from the formula (4). Actually the self-

† *Phys. Rev.* **34** (1929), 661.
‡ *Proc. Camb. Phil. Soc.*, **24** (1927), 89, 111, and 426.
§ *Ibid.*, **23** (1926), 542.
|| *Zeits. f. Physik*, **48** (1928), 73.

consistent field was first used for the calculation of the F-factors† involved in the scattering of X-rays by crystals, and the corresponding values for the scattering of electrons may be obtained from these by means of the relation

$$I(\theta) = \frac{\epsilon^4}{4m^2v^4}(Z-F)^2 \operatorname{cosec}^4\tfrac{1}{2}\theta \tag{11}$$

obtained in Chap. VII, eq. (8). In Table II the values of $I(\theta)$ calculated

TABLE II

$I(\theta)$ calculated from Hartree Fields.

To obtain cross-sections in absolute units multiply by $5\cdot66\times10^{-20}$.

$\dfrac{\sin\frac{1}{2}\theta}{\lambda}\times10^{-8}$	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1
$\sqrt{\text{Volts}}\sin\frac{1}{2}\theta$	1·22	2·45	3·67	4·90	6·12	7·35	8·57	9·80	11·02	12·25	13·47
Li	6400	900	275	112	64	36	24	15	10	7	5
Be	12100	2760	655	225	108	61	37	23	17	12	8
B	22500	4220	1180	425	196	100	59	35	24	17	13
C	19600	5610	1780	655	295	148	88	53	35	25	18
N	14400	4900	1960	860	415	222	123	74	48	32	23
O	8100	4550	2080	1020	540	295	172	104	67	45	31
F	14400	4900	2560	1240	645	361	210	130	85	56	40
Ne	4900	3900	2180	1220	700	420	256	156	106	72	49
Na	18200	4900	2280	1290	772	470	289	188	126	85	59
Mg	22500	7200	2820	1890	830	515	327	220	149	100	70
Al	40000	10200	3400	1600	900	558	361	237	164	114	83
Si	70000	13200	4150	1830	1000	610	400	275	188	130	94
P	67600	15600	5300	2220	1160	675	436	289	204	144	104
S	57600	17400	6130	2600	1340	770	480	324	222	160	116
Cl	57600	20300	7410	3130	1520	850	530	346	243	173	125
A	48400	18200	7100	3380	1660	930	580	380	268	193	142

in this way are given for a number of atoms as a function of $V^{\frac{1}{2}}\sin\frac{1}{2}\theta$, where V is the electron energy in volts and θ is the angle of scattering. For all atoms the resulting angular distribution falls off uniformly with increase in angle of scattering. At a given velocity of impact the rate of decrease of scattering with angle is greater, the smaller the atomic number of the element concerned.

4.1. *Use of the Thomas-Fermi Field. High-velocity Encounters.*‡

In the method of Thomas and Fermi we introduce the auxiliary variables ϕ, x, defined by

$$Z\epsilon\phi = rV(r)$$
$$x = 2^{13/3}3^{-2/3}\pi^{4/3}m\epsilon^2\hbar^{-2}Z^{1/3}r. \tag{12}$$

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† Cf. James and Brindley, *Zeits. f. Crystall.*, **78** (1931), 470.
‡ Bullard and Massey, *Proc. Camb. Phil. Soc.*, **26** (1930), 556.

Then ϕ satisfies the differential equation

$$\frac{d^2\phi}{dx^2} = \phi^{3/2}x^{-1/2},$$

subject to the boundary conditions

$$\phi(0) = 0, \qquad \phi(\infty) = 0.$$

The quantity x/r defines the reciprocal of an 'atomic radius' which we see is a monotonic function of Z.

The function ϕ has been tabulated by Fermi as a function of x, and so $V(r)$ may readily be obtained from this table and the equations (12). On substitution in the expression for $I(\theta)$ we obtain

$$I(\theta) = \left[\frac{3^{4/3}h^2Z^{1/3}}{2^{17/3}\pi^{2/3}\epsilon\mu}\int_0^\infty \phi(x)\sin\mu x\,dx\right]^2, \tag{13}$$

where $\qquad \mu = 3^{2/3}hv\sin\tfrac{1}{2}\theta/(2^{17/3}\pi^{1/3}\epsilon^2Z^{1/3})$.

Since $\phi(x)$ is independent of Z, we see that $I(\theta)Z^{-2/3}$ is a function of μ only, i.e. of $Z^{-1/3}v\sin\tfrac{1}{2}\theta$ only. As a consequence $I(\theta)$ may be obtained for all atoms, if a table is prepared giving $I(\theta)Z^{-2/3}$ as a function of $Z^{-1/3}v\sin\tfrac{1}{2}\theta$. In general this can only be done by numerical integration; but in the special case of large μ, corresponding to high velocities of impact, an approximate explicit expression for $I(\theta)$ may be obtained. This is[†]

$$I(\theta) \sim \frac{Z^2\epsilon^4\operatorname{cosec}^4\tfrac{1}{2}\theta}{4m^2v^4}\left\{1-6\cdot4\times10^{-4}\left(\frac{\operatorname{cosec}\tfrac{1}{2}\theta}{\beta}\right)^{3/2}Z^{1/2}\right\},$$

where $\beta = v/c$.

This formula shows that for these fast collisions the Rutherford formula is a close approximation. The second term, which represents the effect of the atomic electrons, does not resemble in any way the correction, often applied, of substituting Z^2+Z for Z^2 in the Rutherford formula, but it must be remembered that no inelastic collisions have been taken into account in deriving the result. As an example of the magnitude of the correction, we find that for the scattering of 70-kilovolt electrons by gold atoms the correction[‡] to the Rutherford formula is 25 per cent. for angles of scattering of 20°.

The numerical integration required to tabulate $I(\theta)Z^{-2/3}$ as a function of μ (i.e. of $Z^{-1/3}v\sin\tfrac{1}{2}\theta$) was first begun by Mitchell[§] for a few values of μ and completed over the whole range from $\mu = 0$ to $\mu = 15$ by

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[†] Bullard and Massey, *Proc. Camb. Phil. Soc.*, 26 (1930), 556.
[‡] This correction takes no account of any relativistic effects.
[§] *Proc. Nat. Acad. Sci.*, 15 (1929), 520.

Bullard and Massey.[†] The results of these calculations are embodied in Table III.

TABLE III

Scattered Intensities calculated from the Thomas-Fermi Field.

μ	$\dfrac{\sqrt{\text{Volts}}\sin\frac{1}{2}\theta}{Z^{1/3}}$	$I(\theta)/Z^{2/3}$
		$\times 10^{-18}$ cm.^{2}
0	0	2160
0·03	0·062	2120
0·05	0·104	2010
0·1	0·208	1460
0·2	0·41	678
0·3	0·62	344
0·4	0·83	202
0·5	1·04	122
0·6	1·25	79
0·7	1·46	54
0·8	1·66	44·0
0·9	1·87	29·6
1·0	2·08	18·7
1·5	3·12	6·43
2·0	4·16	2·52
3·0	6·25	0·61
5·0	10·4	0·089
6·0	12·5	0·046
7·0	14·6	0·026
8·0	16·7	0·016
9·0	18·7	0·010
10·0	20·8	0·0064
12·0	25·0	0·0032
15·0	31·2	0·0013

Comparison with the values given by the Hartree field shows that the two methods give equivalent results for the heavier atoms, but disagree for the lighter, particularly for those atoms with abnormal sizes such as the rare gases and the alkali metals. The statistical method naturally takes no account of individual differences between atoms and so does not apply satisfactorily to these atoms.

The calculation of total cross-sections may be carried out by a second numerical integration. It may easily be seen that $QZ^{-2/3}$ is a function of $vZ^{-1/3}$ only. This function is illustrated in Fig. 14; it is important to note that the cross-section is a monotonic function of the velocity.

5. The Validity of Born's First Approximation

Before comparing the results of these calculations with experiment it is important to consider the range of validity of the results.

[†] *Proc. Camb. Phil. Soc.*, **26** (1930), 556.

The exact formula (Chap. II, eq. (17)) for the differential cross-section is

$$I(\theta)\,d\omega = \frac{1}{4k^2}\left|\sum_{n=0}^{\infty}(2n+1)(e^{2i\eta_n}-1)P_n(\cos\theta)\right|^2 d\omega. \tag{14}$$

In Chap. VII, § 2, it was shown that the Born formula can be expanded in the form

$$I(\theta)\,d\omega = \frac{1}{k^2}\left|\sum_{n=0}^{\infty}(2n+1)\zeta_n P_n(\cos\theta)\right|^2 d\omega, \tag{15}$$
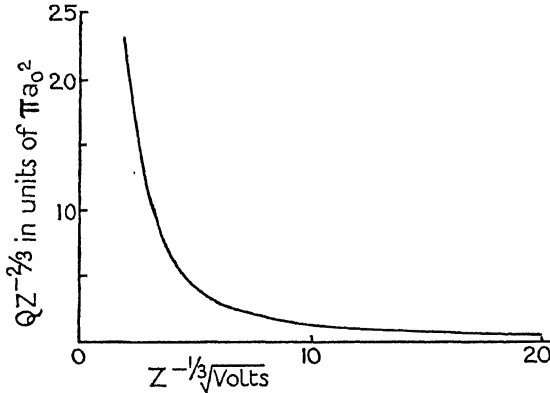
FIG. 14.   Total elastic cross-sections calculated by use of the Thomas-Fermi field.

where

$$\zeta_n = -\frac{4\pi^3 m}{h^2}\int_0^{\infty}V(r)[J_{n+\frac{1}{2}}(kr)]^2 r\,dr. \tag{16}$$

The two formulae will thus give identical results if $\exp(2i\eta_n)-1$ may be replaced by $2i\zeta_n$. This can clearly only be the case if η_n is small, and in Chap. II, § 2, it was shown that under these conditions ζ_n is a good approximation to η_n. We have then, for the condition of accuracy of Born's formula,

$$\frac{4\pi^3 m}{h^2}\int^{\infty}V(r)[J_{n+\frac{1}{2}}(kr)]^2 r\,dr \ll 1 \text{ for all } n. \tag{17}$$

However, this criterion is very severe, for in many cases the expression (14) may involve a large number of terms of the series, and the approximate expression (15) may give all but the first few of these correctly. We may say, then, that when (17) is satisfied there is no possible doubt about the accuracy of the approximation, but when this is not the case the extent of the divergence may not always be great. In general, if

(17) is not very markedly violated for n equal to zero, and if a large number of terms are required, the divergence will be small.

Bearing these considerations in mind, we will consider the applicability of the formula to the scattering of electrons by atoms. Considering first the simplest cases of collisions with hydrogen and helium, we find, using the expressions (8) for $V(r)$ and the approximate formula (16),

$$\zeta_n = \frac{4\pi^2 m\epsilon^2}{kh^2}\left(1 - \tfrac{1}{2}Z\frac{\partial}{\partial Z}\right)Q_n\left(\frac{2Z^2 + k^2 a_0^2}{k^2 a_0^2}\right), \tag{18}$$

where Q_n is the spherical harmonic of the second kind. This gives

$$\zeta_0 = \frac{2\pi^2 m\epsilon^2}{kh^2}\left\{\log\left(1 + \frac{k^2 a_0^2}{Z^2}\right) + \frac{k^2 a_0^2}{Z^2 + k^2 a_0^2}\right\}.$$

In Table IV the numerical values† of η and ζ are given for a number of values of the energy of the incident electrons. In order to estimate the range of validity of the first approximation with more accuracy, an estimate is also given of the number of phases required to give the complete scattering formula (14). This number is estimated by making use of the considerations of Chap. II, § 2, in which it is shown that the contribution of the nth order harmonic is small if

$$\frac{8\pi^2 m}{h^2}V(r) \ll n(n+1)$$

for such r that

$$kr \sim n + \tfrac{1}{2}.$$

TABLE IV

Comparison of Exact and Approximate Expressions for Phases.

Helium.		η_0		η_1		η_2		Number of terms required.
ka_0.	Volts.	Exact.	Born.	Exact.	Born.	Exact.	Born.	
1·05	15	1·360	0·565	0·052	0·042	0·0065	0·0054	1
1·92	50	1·093	0·734	0·186	0·148	0·0411	0·0329	4
3·00	122	0·898	0·731	0·272	0·224	0·0946	0·0769	6
4·00	215	0·784	0·687	0·301	0·264	0·1304	0·1130	8
5·00	340	0·696	0·638	0·308	0·274	0·1524	0·1378	10

Hydrogen.		η_0		Number of terms required.
ka_0.	Volts.	Exact.	Born.	
1·0	13·5	0·905	0·596	1
2·0	54	0·694	0·602	3
3·0	122	0·568	0·534	5
4·0	215	0·490	0·472	6
5·0	340	0·432	0·422	8

† Calculated by Macdougall, *Proc. Roy. Soc.*, A, **136** (1932), 549.

It will be seen that, although the approximate formula for the zero-order phase is not accurate to 10 per cent. below 340 volts in helium and 100 volts in hydrogen, one would expect the complete expansion (15) to be fairly accurate to somewhat lower voltages, say 100 volts in helium and 75 in hydrogen. This is in agreement with the available experimental evidence which is discussed in § 3.1 of this chapter, and also in Chap. XII, § 3, for molecular hydrogen.

For heavy atoms the phases may be approximately calculated from (16) by numerical integration, using the Fermi or Hartree fields. In this way we obtain the following values of ζ_0 for the heavier rare gases at two different voltages.

TABLE V

	Voltage.	ζ_0	n	Voltage.	ζ_0	n
Neon	20	4·5	2	2,000	2·0	10
Argon	30	5·6	4	3,000	2·9	20
Krypton	48	8·8	5	4,800	4·65	30
Xenon	64	11·5	6	6,400	6·1	40

n = approximate number of terms required in series of partial cross-sections.

The approximate number of terms required in the expression (14) is also given for the different cases. From these figures we expect that Born's formula should still be fairly accurate at about 1,000 volts in neon and argon and possibly also in krypton, whereas xenon is more doubtful. For a very heavy atom, such as mercury, we find $\zeta_0 = 8\cdot0$ for 8,000-volt electrons, showing that the first approximation cannot be expected to hold except for very high energy electrons. It must be pointed out again here, however, that ζ_0 itself does *not* have to be less than unity in order that the complete formula may be fairly correct.

5.1. *Higher Approximations in Born's Method.*

The higher approximations in Born's theory have been considered by Møller[†] and by Distel[‡] with the aim of determining the limits of validity of the first approximation, but neither have obtained explicit expressions for even the second approximation. However, Distel has considered also the effect of the inelastic scattering on the elastic,[§] and has shown that, for hydrogen, Born's series of approximations only converges when the velocity v of the incident electron is great

† *Zeits. f. Physik,* **66** (1930), 513.
‡ Ibid. **74** (1932), 785.
§ See also Chap. X, § 10.

compared with the orbital velocity u of the atomic electron. The series
of approximations is virtually an expansion in powers of u^2/v^2. For
heavy atoms it would appear that v refers to the orbital velocity of
the K-electrons, but as the scattering by these two electrons is small
compared with that of the nucleus and remaining electrons, a much
lower orbital velocity can be used in determining the validity of the
first approximation.

A simple method of improving the accuracy of the first approxima-
tion immediately suggests itself when the approximate phases calculated
as above are compared with the correct ones. Referring to Table IV,
we see that the exact zero-order phases do not differ appreciably from
the approximate phases until $\eta_0 > 0.5$. Thus the phases are given
accurately by the approximate formula even when one cannot legiti-
mately make the approximation

$$\exp(2i\zeta_n)-1 \simeq 2i\zeta_n.$$

We therefore obtain an improved result by calculating the larger phases
by the approximate method and correcting the formula for the devia-
tion of $\exp(2i\zeta_n)$—from $2i\zeta_n$.

This gives the formula

$$I(\theta)\,d\omega = \overline{I_b(\theta)}+\frac{1}{2ik}\sum_{n=0}^{\infty}(2n+1)\{\exp(2i\zeta_n)-1-2i\zeta_n\}P_n(\cos\theta)\quad d\omega,$$

(19)

where I_b is the scattered intensity given by the Born formula.

We see from this formula that deviations from Born's formula will
be first noticeable at large angles, for I_b falls off rapidly with increasing
θ, whereas the correcting terms will be less dependent on angle, con-
sisting mainly of contributions from the first few harmonics. The
influence of the corrections will then be most noticeable when θ is
large.

In particular, for the case of helium, we see by reference to Table IV
that Born's formula requires correction for the zero-order term even
when the electron energy is as great as 340 volts. The formula (19)
becomes, for this case,

$$I(\theta)\,d\omega = \sqrt{I_b(\theta)}+\frac{1}{2ik}(e^{2i\zeta_0}-1-2i\zeta_0)\quad d\omega.$$

(20)

For these relatively high velocities $I_b(\theta)$ is very small at large angles
and the scattering should then be given by the second term in (20).
This term does not vary with angle, and so the scattering should deviate
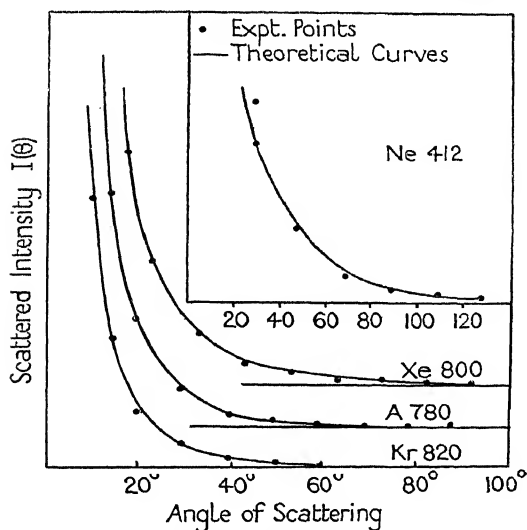
FIG. 15 (*a*). Small angle scattering.
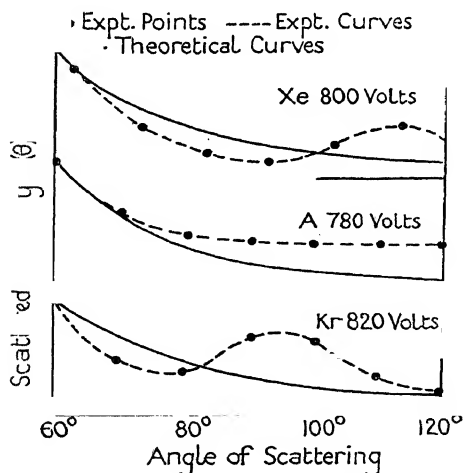
FIG. 15 (*b*). Large angle scattering.
Angular distributions of electrons scattered by rare gas atoms.

from that predicted by Born's formula by remaining nearly constant at large angles instead of falling off uniformly. Referring to Fig. 13, we see that this is just the way in which the observed curves do deviate

from Born's formula (9). The magnitude of the deviation is also approximately correct.

5.2. *Comparison with Experiment.*

For the rare gases the validity of Born's formula may be checked accurately from the measurements of Arnot.† It is found that the formula is accurate down to 400 volts in neon over the complete angular range investigated (15°–120°), whereas for argon, krypton, and xenon the formula represents the observations very well up to angles of 80°. For greater angles of scattering small deviations may be observed for these heavy gases. This is illustrated in Figs. 15 (*a*) and 15 (*b*). As the energy of the incident electrons is decreased the angular range of validity of the formula decreases. Thus at 200 volts in neon the formula fails beyond 90°. The agreement between theory and experiment is thus very satisfactory. Further evidence is afforded by the measurement of the intensities of electron diffraction by metal foils, the intensity distribution in the various orders agreeing well with that calculated by these methods.‡ The use of Born's first approximation for high-velocity electrons finds support also from the measurements of Wierl on the scattering of electrons by molecular vapours discussed in Chap. XII, § 4.

† *Proc. Roy. Soc.*, A, **133** (1931), 615.
‡ Mott, *Nature*, **124** (1929), 986; Mark and Wierl, *Zeits. f. Physik*, **60** (1930), 741; G. P. Thomson, *The Wave Mechanics of the Free Electron* (1931).

ELASTIC SCATTERING OF SLOW ELECTRONS BY ATOMS

1. The Ramsauer and Townsend Effects

As was shown in Chap. IX, § 5, Born's first approximation is not applicable to low-velocity collisions of electrons with atoms, and the experimental results obtained in this region show clearly that a more elaborate theory is required.

In a preliminary investigation in 1921 of the free paths of electrons of very low velocity (0·75 to 1·1 volts) in various gases, Ramsauer† found the free paths of these electrons in argon to be very much greater than that calculated from gas-kinetic theory. The extension of these observations to a wider range of velocities‡ revealed a surprising variation in the cross-section. It was found that the effective cross-section (proportional to the reciprocal of the free path) of argon atoms increases with decreasing velocity until the electron energy becomes less than 10 volts. For electron energies below this value it decreases again to the low values found in the preliminary measurements. Independently, Townsend and Bailey§ examined the variation of free path with velocity for electrons with energies between 0·2 and 0·8 volts by a different method, and showed that a maximum of the free path occurs at about 0·39 volts. This was confirmed by much later work of Ramsauer and Kollath.‖

Since these classical experiments were carried out, the behaviour of a large number of gases and vapours has been examined over a wide voltage range.†† The results obtained are illustrated in Fig. 16 for some monatomic gases and vapours. In these figures the variation of effective cross-section with velocity is illustrated. This is proportional to the reciprocal of the mean free path. For purposes of comparison the gas-kinetic cross-section is indicated on the figures.

The striking features of the cross-section–velocity curves are their wide variation in shape and size and also the marked similarity of behaviour of similar atoms, such as those of the heavier rare gases and the alkali metal vapours. At the time of the earlier measurements no satisfactory explanation of the phenomena could be given, but on the introduction of quantum mechanics it was immediately suggested that

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† *Ann. der Phys.*, **64** (1921), 513.　　　　　‡ Ramsauer, Ibid. **66** (1921), 545.
§ *Phil. Mag.*, **43** (1922), 593; **44** (1922), 1033.
‖ *Ann. der Phys.*, **3** (1929), 536.
†† See, for example, the summary by R. Kollath in *Phys. Zeits.*, **31** (1931), 985.

the effect was a diffraction phenomenon. Thus Bohr† suggested in general terms how the minimum cross-section observed in the rare gases near 0·7 volts could be explained. The field of a rare gas atom falls off very much more rapidly with distance than that of any other atom,
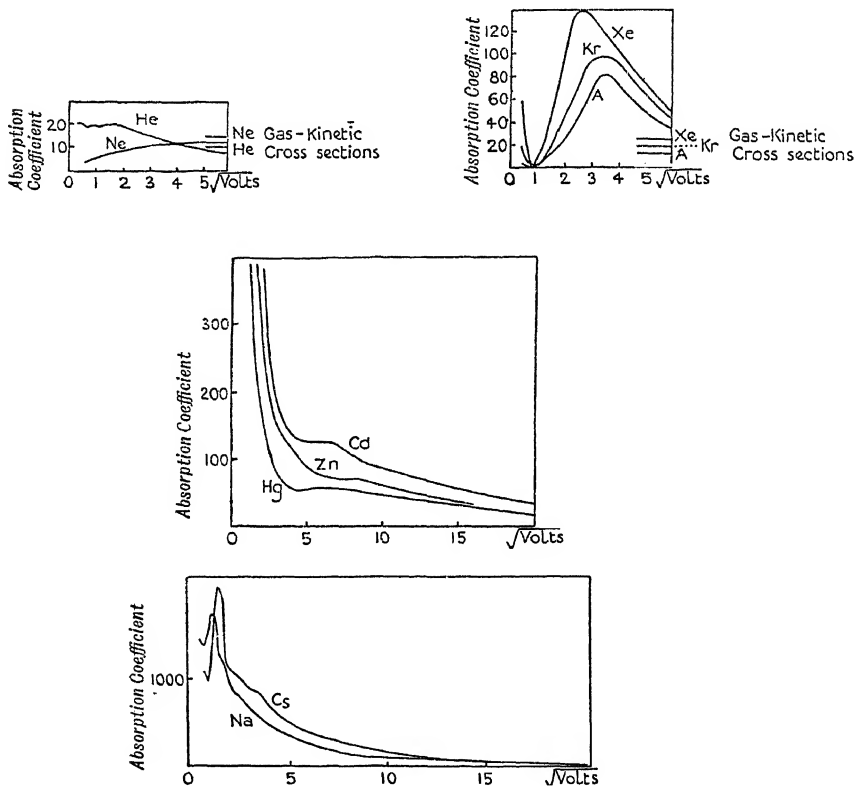
FIG. 16. Observed variation of effective cross-section with electron velocity.

and so an electron wave of long wave-length falling on the atom encounters a region of rapidly increasing refractive index and consequent rapid decrease of wave-length. The result may be that an integral number of wave-lengths are fitted into the region occupied by the scattering field, and the wave passes out from the field unaffected. This will be discussed in greater detail below (§ 2).

Strong experimental evidence of the wave nature of the phenomena was afforded by measurements of the angular distributions of the

† In conversation with Professor R. H. Fowler.

elastically scattered electrons. These were first carried out for electrons of energy between 4 and 40 volts by Bullard and Massey for argon.†
Instead of the curves characteristic of Born's first approximation,
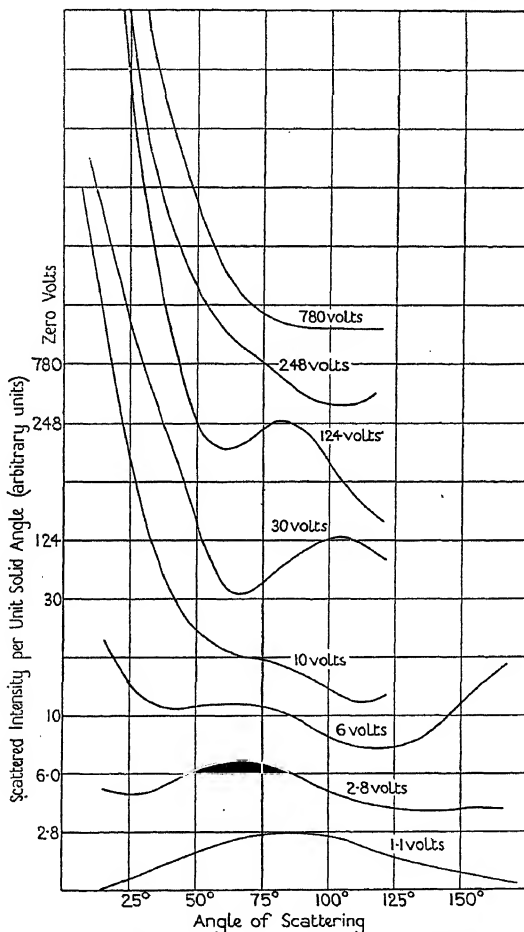
FIG. 17. Observed angular distributions of electrons scattered elastically by argon atoms.

showing a monotonic decrease of intensity with angle of scattering, the curves obtained by Bullard and Massey exhibit maxima and minima. In Fig. 17 a series of curves is given illustrating the variation in form of these curves, for argon, as the electron velocity increases from 1·1 volts

† *Proc. Roy. Soc.*, A, **130** (1931), 579.

to 780 volts; they show the gradual transition to the curves predicted by Born's first approximation. The higher voltage measurements (42–780 volts) are due to Arnot,† and at the lowest voltages (1·1 and 2·8 volts) to Ramsauer and Kollath.‡ These experiments have now been carried out for a large number of gases over a wide range of electron energies, and it is found that in the majority of cases maxima and minima occur in some voltage range.§ For light gases, such as hydrogen and helium, this range is small (up to 15 volts in helium and 6 volts
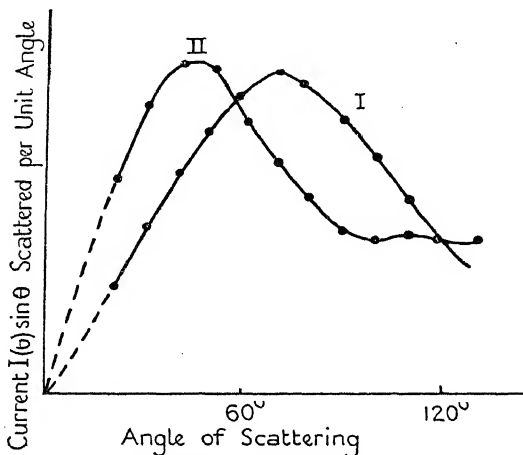
Fig. 18. Illustrating the finite scattering through small angles. I. Curve for 6-volt electrons scattered by neon atoms. II. Curve for 7-volt electrons scattered by nitrogen molecules.

in hydrogen), while for mercury pronounced maxima and minima are observed up to the highest voltages for which observations have been taken (800 volts). From these experiments it is obvious that the wave nature of the electron is important over a wider range than is apparent from the observation of effective cross-sections.

It is of interest to examine the evidence from the angular distribution measurements as to the validity of the theoretical result (Chap. VII,

† *Proc. Roy. Soc.*, A, **133** (1931), 615.
‡ *Ann. der Physik*, **12** (1932), 529.
§ Bullard and Massey, *Proc. Roy. Soc.*, A, **130** (1931), 579, and **133** (1931), 637; Arnot, *Proc. Roy. Soc.*, A, **130** (1931), 655; **133** (1931), 615 and **140** (1933), 334; Pearson and Arnquist, *Phys. Rev.*, 37 (1931), 970; Ramsauer and Kollath, *Ann. der Physik*, **12** (1932), 529 and 837; Hughes and McMillen, *Phys. Rev.*, 39 (1932), 585, and **41** (1932), 39; Tate and Palmer, *Phys. Rev.*, **40** (1932), 731; Mohr and Nicoll, *Proc. Roy. Soc.*, A, **138** (1932), 229, and **138** (1932), 469; Jordan and Brode, *Phys. Rev.*, 43 (1933), 115; Childs and Massey, *Proc. Roy. Soc.*, A, in course of publication.

§ 1.1) that the function $2\pi I(\theta)\sin\theta$, giving the number of electrons scattered per unit *angle* by a gas atom, tends to zero as θ tends to zero. In Fig. 18 two experimental curves representing scattering per unit angle are illustrated, and it is seen that the evidence is in favour of the theoretical conclusion.

2. The Theory of the Scattering of Low-velocity Electrons. Method of Partial Cross-sections

In order to develop a theory of the scattering of low-velocity electrons by atoms, we must refer to the general theory of Chapter VIII. The wave function Ψ, which in this case represents the system of atom + incident electron, was expanded in the form

$$\Psi = \left(\sum_n + \int\right)\psi_n(\mathbf{r}_a)F_n(\mathbf{r}),$$

where $\psi_n(\mathbf{r}_a)$ is the wave function representing the nth excited state of the atomic system. It was then shown that the function $F_n(\mathbf{r})$ satisfies the equation

$$(\nabla^2 + k_n^2)F_n = \frac{8\pi^2 m}{h^2}\int V(\mathbf{r}, \mathbf{r}_a)\Psi(\mathbf{r}_a, \mathbf{r})\psi_n^*(\mathbf{r}_a)\,d\tau_a,$$

where $V(\mathbf{r}, \mathbf{r}_a)$ is the interaction energy between the incident and atomic electrons, and k_n is the wave number of the outgoing electron wave, equal to $2\pi m v_n/h$.

If we neglect electron exchange, the elastic scattering is completely determined by the function F_0, which satisfies the equation

$$(\nabla^2 + k^2)F_0(\mathbf{r}) = \frac{8\pi^2 m}{h^2}\int V(\mathbf{r}, \mathbf{r}_a)\Psi(\mathbf{r}_a, \mathbf{r})\psi_0^*(\mathbf{r}_a)\,d\tau_a. \tag{1}$$

To solve (1) we must substitute some approximate form for Ψ on the right-hand side of (1). For instance, in obtaining Born's approximation in Chapter IX we neglected all the scattered waves, and replaced Ψ by $\psi_0(\mathbf{r}_a)\exp(ikz)$. In the approximation, to the examination of which this chapter is devoted, we neglect all but the elastically scattered wave, and thus set on the right-hand side of (1)

$$\Psi = \psi_0(\mathbf{r}_a)F_0(\mathbf{r}).$$

We thus obtain $$\left\{\nabla^2 + k^2 - \frac{8\pi^2 m}{h^2}V_{00}(r)\right\}F_0(\mathbf{r}) = 0, \tag{2}$$

where $$V_{00}(r) = \int V(\mathbf{r}, \mathbf{r}_a)\psi_0\psi_0^*\,d\tau_a.$$

This is the equation which represents the motion of the incident electron in the static field of the atom, V_{00} being just the potential of this field.

We have thus, to this approximation, reduced the problem to that of calculating the scattering by the static field of the atom concerned. The method required for this calculation is described in Chap. II, § 1. Since we shall have no further occasion to consider the inelastic scattering in this chapter, we shall drop the suffix $_0$ in F_0 and V_{00}.

If we expand the function F in the form

$$F = \sum_s F_s(r)P_s(\cos\theta),$$

and substitute in (2), the function $F_s(r)$ satisfies the equation

$$\frac{d^2}{dr^2}(rF_s) + \left[k^2 - \frac{8\pi^2 m}{h^2}V(r) - \frac{s(s+1)}{r^2}\right](rF_s) = 0. \tag{3}$$

As shown in Chapter II, the solution of this equation, which is finite at the origin, will have the asymptotic form

$$rF_s \sim A_s\sin(kr - \tfrac{1}{2}s\pi + \eta_s),$$

η_s being a phase constant. The amplitude $f(\theta)$ of the scattered wave was shown in Chapter II to be given by

$$f(\theta) = \frac{1}{2ik}\sum_{s=0}^{\infty}(2s+1)[\exp(2i\eta_s) - 1]P_s(\cos\theta), \tag{4}$$

and the differential cross-section for elastic scattering into the solid angle $d\omega$ is

$$I(\theta)\,d\omega = |f(\theta)|^2\,d\omega.$$

The total elastic cross-section Q is given by

$$Q = 2\pi\int_0^\pi I(\theta)\sin\theta\,d\theta;$$

we thus obtain

$$Q = \sum_s Q_s,$$

where

$$Q_s = 4\pi k^{-2}(2s+1)\sin^2\eta_s. \tag{5}$$

We refer to Q_s as the partial cross-section of order s.

The calculation of the cross-sections $I(\theta)$ and Q thus involves the calculation of the phase-shifts η_s of the various scattered waves. Born's first approximation holds only when η_s is small, so that $\sin\eta_s$ never passes through a maximum due to η_s reaching the value $\tfrac{1}{2}\pi$. Thus to this approximation one expects no oscillations in Q_s as a function of the energy, but this is no longer the case if η_s may become greater than $\tfrac{1}{2}\pi$.

3. Convergence of Series of Partial Cross-sections

It was proved in Chap. VII, § 2, that the series of partial cross-sections is convergent, and in Chap. II, § 2, a method of estimating the number

of terms required was described. This method depends on the fact that the partial cross-section Q_s corresponds to particles with quantized angular momenta $\{s(s+1)\}^{\frac{1}{2}}h/2\pi$. It was shown that, if

$$V(r) \ll \frac{s(s+1)}{r^2} \frac{h^2}{8\pi^2 m},$$

for r given by

$$kr \sim \{s(s+1)\}^{\frac{1}{2}} \qquad (k = 2\pi mv/h),$$

the contribution of all phases η_n with $n > s$ can be neglected. Hence the convergence will be best for light atoms and slow electrons. In particular, at the low-velocity limit the scattering arises entirely from the zero-order terms. For light atoms the convergence of the series of partial cross-sections is rapid for all velocities lower than those for which Born's approximation is valid. However, for such heavy atoms as mercury there is an intermediate range of velocities where Born's approximation is far from satisfactory, and where also the convergence of the series is very slow. The method used for such cases is discussed in Chap. XIII, § 3.1.

4. The Low-velocity Limit of the Collision Cross-section

As mentioned above, the collision cross-section of the heavier rare gas atoms for impacts with very slow electrons (0·5 volts) has been observed by Ramsauer, and by Townsend and Bailey, to be much smaller than the gas-kinetic value. As we have seen, for such slow electrons, Q is practically equal to the zero-order cross-section, Q_0. In order to explain the experimental facts, we must therefore find under what conditions $Q_0 \to 0$ as λ, the wave-length, tends to infinity. This was first done by Faxén and Holtsmark,† whose method we now describe.

The plane wave e^{ikz} may be expanded in spherical harmonics, the first term of the expansion being $\sin kr/kr$. We have seen that the scattered wave is spherically symmetrical; outside the atom we may therefore take it to be $c_0 r^{-1} e^{ikr}$. Thus at points outside the atom, but for r much less than the wave-length, the complete wave function is

$$\sin kr/kr + c_0 r^{-1} e^{ikr}. \tag{6}$$

Inside the atom let the wave function be $F_0(r)$; F_0 is the solution of the differential equation (3) which is finite at the origin, and is thus determined except for an arbitrary multiplying constant. The quantity F_0'/F_0 is thus determined uniquely by the equation, for all r.

We imagine for the moment that the atom has a fixed boundary

† *Zeits. f. Physik*, **45** (1927), 307.

$r = R$. Then we determine c_0 by fitting (6) to F_0 at $r = R$. We obtain

$$\frac{\cos kR + c_0\, ike^{ikR}}{k^{-1}\sin kR + c_0\, e^{ikR}} = \left[\frac{(rF_0)'}{(rF_0)}\right]_{r=R}.$$

The right-hand side is a known quantity; we may therefore solve for c_0. We are interested in the case of long wave-length ($k \to 0$). Thus, solving and making $k \to 0$, we obtain

$$\lim_{k\to 0} c_0 = -R^2 F_0'/(RF_0' + F_0).$$

Thus, if for very long wave-length F_0' is zero at the boundary of the atom, c_0 is zero and the cross-section vanishes.

This is really the mathematical statement of Bohr's explanation of the Ramsauer-Townsend effect discussed in § 1, for if this condition is satisfied, the atomic field has simply the effect of introducing an additional complete oscillation of the wave function of the incident particle. The effect can only occur for atomic fields which are strong enough to produce an additional zero in the wave function. It cannot therefore occur for *repulsive* fields. The reason why the heavier rare gases are most effective in exhibiting the Ramsauer-Townsend effect is that the fields of these atoms are very sharply defined and produce a rapid change of wave-length in the zero-order wave, while the higher orders are not effective.

Faxén and Holtsmark (loc. cit.) have tested this theory by evaluating the function F_0 for various fields by numerical methods. They found that the hydrogen atom is too small to produce the effect, but that fields closely resembling that of the argon atom can be effective. However, the main interest of the calculation is that it shows how the effect can·occur.

5. General Application of Method of Partial Cross-sections

We have shown that the theory is capable of explaining the observed small values of the collision cross-sections; we shall now attempt to extend its application to all other cases of collisions of slow electrons with atoms.

We have to give a general explanation of the following experimental facts:

1. The magnitude of the cross-section varies between wide limits, the maximum observed for the alkali metals being over 100 times that observed in neon.

2. The angular distributions of the scattered electrons show marked maxima and minima.

   3. The cross-section–velocity curves have forms characteristic of the different columns of the periodic table.

In order to do this we make use of the following properties of the calculated phases:

   (a) For any atomic field η_s decreases monotonically with s.

   (b) η_s is small when, for r such that $kr \sim s + \frac{1}{2}$,

$$\frac{8\pi^2 m}{h^2} V(r) \ll \frac{s(s+1)}{r^2}.$$

It follows from (b) that the series of partial cross-sections will converge quite quickly for low-velocity impacts; the major contribution will arise from the partial cross-sections Q_s of such an order that $\eta_s \simeq \frac{1}{2}\pi$. The maximum value of the contribution from a partial cross-section of order s is

$$Q_s^{\max} = \frac{4\pi}{k^2}(2s+1).$$

We may therefore say at once that, the lower the velocity and the larger the value of s for which the phase η_s attains the value $\frac{1}{2}\pi$, the bigger will be the cross-section. Referring to the condition (b), we see that the biggest collision cross-sections will be those of atoms whose fields extend out to the greatest distances, viz. the alkali metals. If we use the empirical rules due to Slater† for the effective nuclear charges of alkali atoms, and define the diameter of an atom as the distance at which the radial charge density $r^2|\psi|^2$ of the outer shell is a maximum, the following values of the radii r_0 of various atoms are obtained:

TABLE I

	r_0 in atomic units.	kr_0	
		13 volts.	0·5 volts.
Li	2·3	2·3	0·46
Ni	4·1	4·1	0·82
K	6·1	6·1	1·22
Zn	3·1	3·1	0·62
He	0·6	0·6	0·12
Ne	0·7	0·7	0·14
A	1·3	1·3	0·26
Kr	1·7	1·7	0·34

Note. k is measured in units of $1/a_0$.

We give also the values of kr_0 corresponding to 13- and 0·5-volt electrons. Thus, using the criterion (b), we find that for potassium at

† *Phys. Rev.*, **36** (1930), 57.

least 7 harmonics are required, and the cross-section may be greater than† $50\pi a_0^2$, whereas one harmonic only is required for neon, and the effective area will not be greater than $10\pi a_0^2$. For $k = 0\cdot2/a_0$ ($0\cdot54$ volts), the area may be as great as $300\pi a_0^2$ for potassium, but still not much greater than $10\pi a_0^2$ for neon or helium. There is, then, clearly no difficulty in explaining the wide range in magnitude observed in the effective cross-sections. It is equally clear that the method indicates the possibility of maxima and minima in the angular distribution given by (4). Again the dominant effect arises from terms in the series such that $\eta_s \simeq \frac{1}{2}\pi$. The angular distribution, then, is roughly of the form

$$I(\theta) = \text{const.}\{P_s(\cos\theta)\}^2,$$

which has s minima. This will be especially marked for the lower velocity impacts, where only a few terms of the series (4) are required and the weight factor $2s+1$ is particularly effective. Thus for electrons of 30 volts energy in argon the angular distribution is given closely by $\{P_2(\cos\theta)\}^2$. Actually the calculated phase values at this velocity are

$$\eta_0 = 2\pi + 0\cdot885, \quad \eta_1 = 4\cdot831, \quad \eta_2 = 1\cdot983, \quad \eta_3 = 0\cdot374, \quad \eta_4 = 0\cdot159.$$

It must be realized that these remarks are only illustrative, and the actual effects produced by the sum of a number of partial cross-sections may be very complicated, particularly for heavy atoms. The diffraction of waves by spherical obstacles is a much more complicated process than diffraction by a grating or other symmetrical arrangement.

It is not possible to explain the third feature listed above in such simple terms as the preceding. The quasi-periodic behaviour of the partial cross-sections must be due to the behaviour of $\sin\eta_s$. At low velocities, for the lightest atoms, only the zero-order phase is appreciable. For some atomic field this phase will attain a value near $\frac{1}{2}\pi$ and the corresponding cross-section will pass through a maximum. Again, for some heavier atom a value of $\frac{3}{2}\pi$ will be attained, giving an equal maximum of the zero-order cross-section, and so on. For some atom with intermediate properties η_1 will become appreciable, and so on. In this way some quasi-periodic behaviour of the cross-sections might be expected, but we still require to show from the theory that the periodicity follows that of the periodic table. This was first done by Allis and Morse‡ using a simplified atomic model. They took for the atomic field

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† The cross-sections obtained in this way will only be approximately correct when the field is sufficiently strong to produce large phase changes. For collisions of high-velocity electrons a large number of terms are required in the series, but each is small and the total cross-section small also.

‡ *Zeits. f. Physik*, **70** (1931), 567.

the form

$$= 2Z\left(\frac{1}{r} - \frac{1}{r_0}\right) \qquad (r \leqslant r_0),$$

$$= 0 \qquad\qquad\qquad (r \geqslant r_0), \qquad (7)$$

which makes possible an analytic solution of equation (3). In order to illustrate the periodic behaviour of the cross-sections two quantities, x and β, were defined such that

$$\beta^2 = Zr_0/2, \qquad x = kr_0.$$

The first of these depends only on the atomic field, while the second is a function also of the incident electron velocity. Allis and Morse then
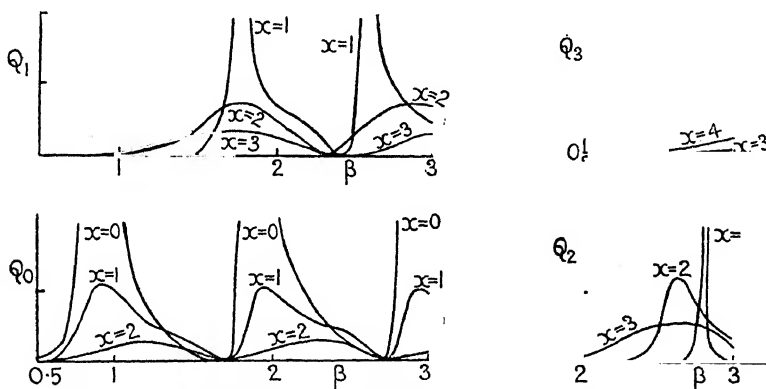
FIG. 19. Illustrating quasi-periodicity of partial cross-sections.

showed that the cross-sections are quasi-periodic in β with period unity. This is illustrated in Fig. 19, where a number of partial cross-sections corresponding to different values of x are illustrated as functions of β. If, now, the approximate atomic radii given by Slater are used (given above in Table I) and the constant Z above, adjusted to give as good agreement as possible of the form (7) for V with that obtained from Slater's values, it is found that a period of 1 in β is approximately a whole period in the periodic table. This may be seen from the following values of β:

TABLE II

Lithium	.	.	.	1·36	Helium	.	.	.	0·77
Sodium	.	.	.	2·54	Neon	.	.	.	1·73
Potassium	.	.	.	3·51	Argon	.	.	.	2·68
					Krypton	.	.	.	3·66

The lighter elements are to some extent anomalous in this respect; this is also borne out by the observations (see Fig. 16 of this chapter).

6. Quantitative Application of Method of Partial Cross-sections

The first quantitative application of the theory was made by Holts-mark† for the scattering of electrons by argon; but we shall first con-sider the results obtained by Allis and Morse using their simplified model.

Having chosen the values of the parameter β and r_0, using Slater's rules (loc. cit.), it was usually found that a good approximation to the observed cross-sections is obtained with this model. In Fig. 20 the experi-mental curves are compared with calculated curves. The values of β and r_0 used in obtaining the latter are slightly different from those obtained from Slater's rules (loc. cit.), but the differences are not great.
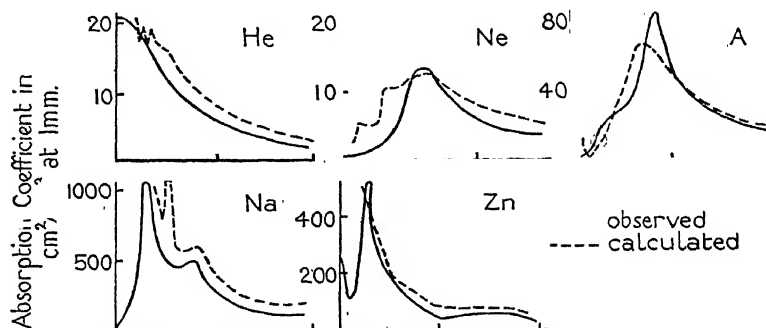
FIG. 20. Illustrating comparison of observed and calculated cross-section curves.

In Table III the parameters which give the best fit with experiment are compared with Slater's values, both measured in atomic units.

TABLE III

Atom.	β		r_0	
	Slater.	From Cross-sections.	Slater.	From Cross-sections.
Helium	0·77	0·80	0·6	0·55
Neon	1·73	1·71	0·7	0·75
Argon	2·68	2·7	1·3	1·4
Sodium	2·54	2·55	4·1	4·25
Zinc	3·77	3·78	3·1	3·14

The agreement obtained is very striking and leaves little doubt as to the correctness of the theoretical explanation of the Ramsauer-Towns-end effects afforded by quantum mechanics. However, the field used gives only a rough approximation, particularly for very low velocity

† *Zeits. f. Physik*, **55** (1929), 437.

collisions.† For such cases large effects may arise from the atomic field beyond the radius r_0.

Holtsmark‡ has obtained very good agreement with the observed cross-section for argon by using the Hartree field and evaluating the phases η_s exactly by numerical integration of the differential equations.

A much stricter test of the theory may be applied by comparing calculated and observed angular distributions. These are much more sensitive to inaccuracy in the theory. In Fig. 21 the angular distribution
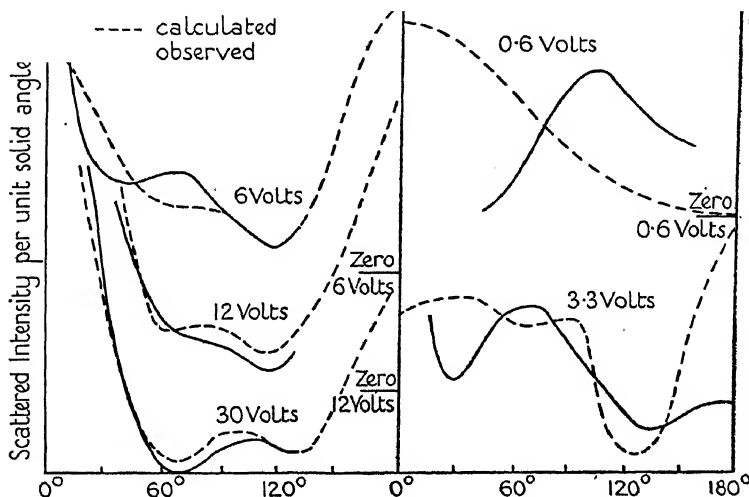
FIG. 21. Comparison of observed and calculated angular distributions of electrons scattered by argon atoms.

curves observed by Bullard and Massey and by Ramsauer and Kollath for argon (loc. cit.) are compared with those calculated by using Holtsmark's values of the phases η_s. The agreement for 30 and 12 volts is found to be extremely good in view of the peculiar nature of the experimental curves. It is of interest to note that at the lower voltages the agreement with curves calculated from the simplified model of Morse and Allis discussed in § 5 is not nearly so satisfactory. At very low velocities, however, the observations of Ramsauer and Kollath are no

† Morse has extended the calculations to the field
$$V = Z \exp(-2r/r_0)r^{-1}$$
and finds that very similar results are obtained. The same quantities β and kr_0 are again important. [*Rev. Mod. Phys.*, 4 (1932), 577.]

‡ Loc. cit.

longer in agreement even with the calculations using Hartree fields, as seen from the figure.

The exact phases have been calculated for only three other atoms, namely, for krypton by Holtsmark† and for helium and hydrogen by Macdougall.‡ For the former the agreement with experiment is again very good, both in comparison with observed total cross-sections and with the angular distributions measured by Arnot§ and by Ramsauer and Kollath,‖ except at very low voltages (less than 3 volts).
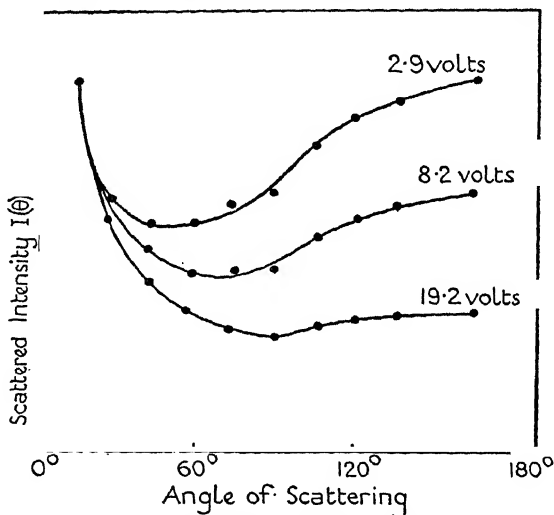
FIG. 22. Observed angular distributions of slow electrons scattered elastically by helium atoms.

In the case of helium we find the first definite indication of a failure of the theory. For such a light atom the only phase which attains a value of $\frac{1}{2}\pi$ is that of zero order, and at electron velocities below 20 volts the effect of the higher-order terms is negligible. The corresponding angular distribution is independent of angle; but the observed curves†† exhibit a minimum when the electron velocity is below 15 volts. This is illustrated in Fig. 22. The presence of this minimum at very low velocities cannot be explained by the method of partial cross-sections, and we must develop the theory further in order to provide an explanation. This is done in § 8. Similar behaviour is observed in molecular

† *Zeits. f. Physik*, **66** (1930), 49.   ‡ *Proc. Roy. Soc.*, A, **136** (1932), 549.
§ Ibid. A, **133** (1931), 615.   ‖ *Ann. der Physik*, **12** (1932), 837.
†† Bullard and Massey, loc. cit.; Ramsauer and Kollath, loc. cit.

hydrogen. It is possible that the effect of the molecular binding is important, but it is much more likely that the reason is the same as that for helium (exchange). This will also be discussed in § 8 below.

Approximate methods may be used to compare the theoretical results with the observations in neon and mercury vapour. For neon the only important term in the series of partial cross-sections, for energies below 100 volts, is the term of order unity, so the theory predicts that the
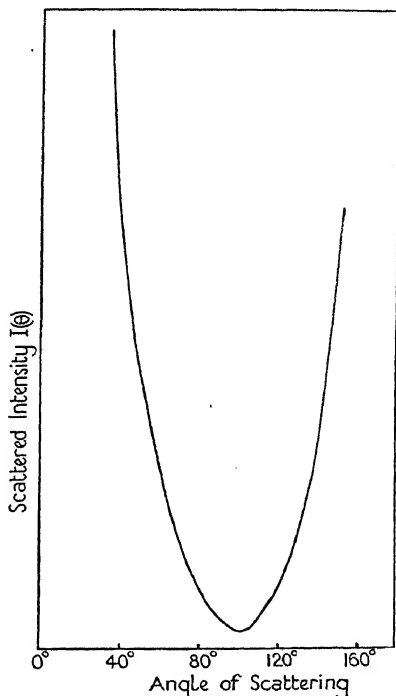
FIG. 23. Observed angular distribution of electrons elastically scattered by neon atoms.

scattered intensity $I(\theta)$ shall vary as $\cos^2\theta$. The experimental results for electrons of not too low energy confirm this. Fig. 23 shows the angular distribution of 80-volt electrons observed by Mohr and Nicoll;[†] there is a deep minimum at 90° and the curve is symmetrical about this axis.

At lower voltages, however, the curves deviate from the form $\cos^2\theta$ in two ways. Firstly, the minimum becomes displaced from 90°; this is due to the effect of the zero-order harmonic. Secondly, a point of

† *Proc. Roy. Soc.*, A, **138** (1932), 469.

inflexion appears for energies below 50 volts, and becomes more marked for decreasing energy. This can hardly be due to higher harmonics, owing to the small range of the neon field, and to the fact that it increases with decreasing energy. It may, however, be due to exchange (cf. § 9).

For mercury vapour calculations have been carried out by Henneberg† and by Massey and Mohr‡ using the approximate method de-
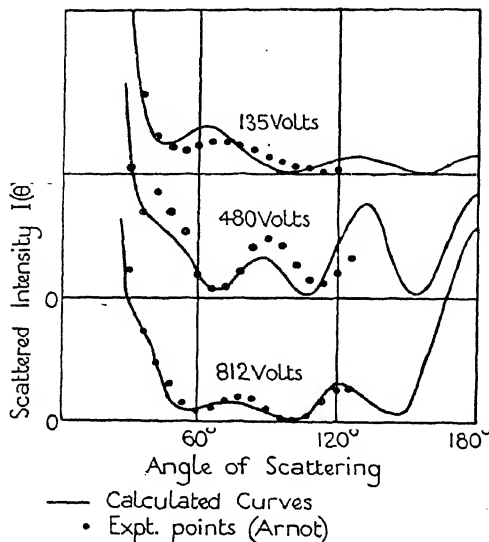
Fig. 24. Comparison of observed and calculated angular distributions of electrons elastically scattered by mercury atoms.

scribed in Chap. XIII, § 3.1, of calculating the large phases by using Jeffrey's approximation and the small ones by Born's method, and interpolating in order to obtain the remainder. In the absence of a Hartree field for mercury the Thomas-Fermi field was used, but for a heavy atom such as mercury this field should be quite a good approximation. The calculated angular distributions are compared with Arnot's observations in Fig. 24. In view of the approximate method used the agreement is very satisfactory, and seems to establish still further the validity of Faxén and Holtsmark's method as applied to the calculation of the elastic scattering of slow electrons by heavy atoms. For light atoms such as helium and hydrogen it is necessary

† *Naturwiss.*, **20** (1932), 561.   ‡ *Nature*, **130** (1932), 276.

to proceed to higher approximations, and in the next section we shall do this. It also appears that the theory becomes invalid in the neighbourhood of the cross-section minimum in the case of the rare gases. The reason for this is not at present clear, but may be due to the same cause as that operative for light atoms, namely, electron exchange.

7. Electron Exchange in Elastic Collisions

In Chap. VIII, § 4, the possibility of electron exchange between the atom and the colliding beam was considered. It was shown that an incident electron may either be directly scattered, or may change places with an atomic electron. It was shown also that the probability of the two processes cannot be added; owing to the necessity for using anti-symmetrical wave functions, one must combine the wave amplitudes rather than their intensities.

The possibility of exchange interference was first pointed out by Oppenheimer,† who suggested that this was the explanation of the minimum observed in the cross-section velocity curves of the heavier rare gases at very low voltages. In view of the theory discussed in § 4 it is unlikely that this view is correct. For light atoms such as helium and hydrogen, however, exchange interference seems to be of considerable importance in low-velocity collisions.

8. Calculation of Effect of Electron Exchange in Elastic Scattering by Hydrogen and Helium

We employ the same notation as that used in Chap. VIII, § 4. It was shown there that the elastic scattering of electrons by atoms of hydrogen and helium may be described by means of two wave functions $F_0(\mathbf{r}_1)$, $G_0(\mathbf{r}_2)$ which have the asymptotic form

$$F_0(\mathbf{r}_1) \sim \exp ikz_1 + r_1^{-1}f_0(\theta_1, \phi_1)\exp ikr_1,$$

$$G_0(\mathbf{r}_2) \sim r_2^{-1}g_0(\theta_2, \phi_2)\exp ikr_2. \tag{8}$$

The differential cross-section for elastic collisions is then

$$I(\theta)\, d\omega = \tfrac{1}{4}\{3|f_0+g_0|^2 + |f_0-g_0|^2\}\, d\omega \quad \text{for hydrogen,}$$

$$= |f_0-g_0|^2\, d\omega \qquad\qquad \text{for helium.}$$

For simplicity let us consider the case of hydrogen first. The functions

† *Phys. Rev.*, **32** (1928), 361.

$F_0(\mathbf{r}_1)$, $G_0(\mathbf{r}_2)$ were shown to satisfy the equations

$$\left.\begin{array}{l}[\nabla^2+k^2]F_0(\mathbf{r}_1) = -\dfrac{8\pi^2 m\epsilon^2}{h^2}\displaystyle\int\left(\dfrac{1}{r_1}-\dfrac{1}{r_{12}}\right)\Psi(\mathbf{r}_1,\mathbf{r}_2)\psi_0^*(\mathbf{r}_2)\,d\tau_2 \\[3mm] [\nabla^2+k^2]G_0(\mathbf{r}_2) = -\dfrac{8\pi^2 m\epsilon^2}{h^2}\displaystyle\int\left(\dfrac{1}{r_2}-\dfrac{1}{r_{12}}\right)\Psi(\mathbf{r}_1,\mathbf{r}_2)\psi_0^*(\mathbf{r}_1)\,d\tau_1 \end{array}\right\}, \quad (9)$$

where the function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ is the wave function for the complete system.

In order to integrate the equations (9) we must assume some approximate form for Ψ on the right-hand side, so that the right-hand side becomes a known function. We know that Ψ may be expanded in the form

$$\Psi = \left(\sum_n + \int\right)F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2).$$

We may write this

$$\Psi = F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+\Phi,$$

where Φ includes all the scattered waves.

Now Ψ may be expanded in the alternative series

$$\Psi = \left(\sum_n + \int\right)G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1),$$

as we saw in Chapter VIII. If we expand Φ in the form

$$\Phi = \left(\sum_n + \int\right)G_n'(\mathbf{r}_2)\psi_n(\mathbf{r}_1),$$

then it is clear that $G_0 = G_0'$; in other words, the 'exchange' wave is included in Φ. Thus, if we assume for Ψ on the right-hand side of (9)

$$\Psi = F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)+\phi, \quad (10)$$

and neglect ϕ, we shall have a fair approximation, which amounts to neglecting the effect of all waves with wave-length different from that of the incident wave.

If we substitute (10) in (9), we obtain

$$\left[\nabla^2+k^2-\frac{8\pi^2 m}{h^2}V_{00}(r_1)\right]F_0(\mathbf{r}_1)$$

$$= -\frac{8\pi^2 m\epsilon^2}{h^2}\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)\psi_0^*(\mathbf{r}_2)\,d\tau_2 \quad (11\,\mathrm{a})$$

and

$$\left[\nabla^2+k^2-\frac{8\pi^2 m}{h^2}V_{00}(r_2)\right]G_0(\mathbf{r}_2)$$

$$= -\frac{8\pi^2 m\epsilon^2}{h^2}\int\left(\frac{1}{r_2}-\frac{1}{r_{12}}\right)F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\psi_0^*(\mathbf{r}_1)\,d\tau_1, \quad (11\,\mathrm{b})$$

where

$$V_{00}(r_1) = -\epsilon^2\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)|\psi_0(\mathbf{r}_2)|^2\,d\tau_2.$$

Changing the variable in G_0 from $\mathbf{r}_2$ to $\mathbf{r}_1$, we obtain, by adding and subtracting (11 a) and (11 b),

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 m}{h^2} V_{00}(r_1)\right]\{F_0(\mathbf{r}_1) \pm G_0(\mathbf{r}_1)\}$$

$$= \mp \frac{8\pi^2 m \epsilon^2}{h^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}}\right)\{F_0(\mathbf{r}_2) \pm G_0(\mathbf{r}_2)\}\psi_0(\mathbf{r}_1)\psi_0^*(\mathbf{r}_2)\,d\tau_2. \quad (12)$$

This 'integro-differential' equation may be converted into an integral equation in the following way. We require a solution of the equation for $F_0 \pm G_0$ which has the asymptotic form

$$F_0(\mathbf{r}) \pm G_0(\mathbf{r}) \sim e^{ikz} + r^{-1}e^{ikr}\{f(\theta, \phi) \pm g(\theta, \phi)\}. \quad (13)$$

Let us then treat the right-hand side of (12) as a known function, $\phi(\mathbf{r}_1)$, of r_1. We may then write

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 m}{h^2} V_{00}(r)\right][F_0(\mathbf{r}) \pm G_0(\mathbf{r})] = \mp\phi(\mathbf{r}). \quad (14)$$

The solution of this type of inhomogeneous equation has been discussed in Chap. VI, § 3. Let $\mathfrak{F}(r, \theta)$ be the solution of the homogeneous equation

$$\left[\nabla^2 + k^2 - \frac{8\pi^2 m}{h^2} V_{00}(r)\right]\mathfrak{F}(r, \theta) = 0, \quad (15)$$

which has the asymptotic form

$$\mathfrak{F}(r, \theta) \sim e^{ikz} + (2ikr)^{-1}e^{ikr}\sum_s (2s+1)[\exp(2i\eta_s) - 1]P_s(\cos\theta), \quad (16)$$

corresponding to an incident plane wave and a diverging spherical wave (the method of obtaining such a solution is given in Chapter II); then the asymptotic form of the required solution of (14) is

$$F_0(\mathbf{r}) \pm G_0(\mathbf{r}) \sim \mathfrak{F}(r, \theta) \pm r^{-1}e^{ikr}\frac{1}{4\pi}\int \phi(\mathbf{r}')\mathfrak{F}(r', \pi-\Theta)\,d\tau',$$

where Θ denotes the angle between the vectors $\mathbf{r}$, $\mathbf{r}'$.

Substituting in (12), we obtain

$$F_0(\mathbf{r}) \pm G_0(\mathbf{r}) \sim e^{ikz} + (2ikr)^{-1}e^{ikr}\sum_s (2s+1)[\exp(2i\eta_s) - 1]P_s(\cos\theta)$$

$$\pm \frac{e^{ikr}}{r}\frac{2\pi m \epsilon^2}{h^2}\int\int \left(\frac{1}{r_1} - \frac{1}{r_{12}}\right)\{F_0(\mathbf{r}_2) \pm G_0(\mathbf{r}_2)\}\psi_0(\mathbf{r}_1)\psi_0^*(\mathbf{r}_2)\mathfrak{F}_0(r_1, \pi-\Theta)\,d\tau_1\,d\tau_2,$$

$$(17)$$

where Θ is the angle between $\mathbf{r}$, $\mathbf{r}_1$. The significance of the various terms in this formula is interesting. The first is the incident plane wave, the second the wave scattered by the static field $V_{00}(r)$ of the atom, while the third is the scattered wave due to electron exchange. The

calculation of the amplitude of the first type of scattered wave has been considered in the preceding section, and we are now concerned with the second.

We must introduce further approximations in order to calculate the effect of exchange. In two cases we may do this without difficulty. They are as follows:

(1) Effect of atomic field small, so that the incident wave may be taken as approximately plane. In this case we set on the right-hand side of (17)

$$F_0(\mathbf{r}) - G_0(\mathbf{r}) = \exp(ik\mathbf{n}_0 \cdot \mathbf{r})$$
$$\mathfrak{F}(r_1, \pi - \Theta) = \exp(-ik\mathbf{n} \cdot \mathbf{r}_1),$$

where $\mathbf{n}_0$, $\mathbf{n}$ are unit vectors in the direction of incidence and of scattering (i.e. θ, ϕ), respectively. This gives for the exchange amplitude

$$g(\theta) = \frac{2\pi m\epsilon^2}{h^2} \int \int \left(\frac{1}{r_1} - \frac{1}{r_{12}}\right) \exp\{ik(\mathbf{n}_0 \cdot \mathbf{r}_2 - \mathbf{n} \cdot \mathbf{r}_1)\} \psi_0(\mathbf{r}_1)\psi_0^*(\mathbf{r}_2)\, d\tau_1 d\tau_2. \quad (18)$$

(2) Effect of exchange small compared with direct scattering. In this case we may take on the right-hand side of (17)

$$F_0(\mathbf{r}_2) - G_0(\mathbf{r}_2) = \mathfrak{F}_0(r_2, \theta_2),$$

and we have for the exchange amplitude

$$g(\theta) = \frac{2\pi m\epsilon^2}{h^2} \int \int \left(\frac{1}{r_1} - \frac{1}{r_{12}}\right) \mathfrak{F}_0(r_2, \theta_2)\mathfrak{F}_0(r_1, \pi - \Theta)\psi_0^*(\mathbf{r}_2)\psi_0(\mathbf{r}_1)\, d\tau_1 d\tau_2. \quad (19)$$

For helium similar formulae may be obtained. Since in this case only the antisymmetrical cross-section is required, it is possible to make a third approximation. The effect of electron exchange is to reduce the amplitude of the scattered wave so that, in a certain energy range where $f(\theta)$ and $g(\theta)$ are of comparable magnitude, we may replace $F_0 - G_0$ on the right-hand side of (17) by a plane wave, and obtain

$$g(\theta) = \frac{2\pi m\epsilon^2}{h^2} \int \int \int \left(\frac{2}{r_1} - \frac{1}{r_{12}} - \frac{1}{r_{13}}\right) \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_2) \times$$
$$\times \mathfrak{F}_0(r_1, \pi - \Theta)\psi_0(\mathbf{r}_1, \mathbf{r}_3)\psi_0^*(\mathbf{r}_2, \mathbf{r}_3)\, d\tau_1 d\tau_2 d\tau_3. \quad (20)$$

Unfortunately we are not on very safe ground in doing this since, although the amplitude of the scattered wave is small at infinity, the deviations of $F_0 - G_0$ from the plane wave form may be important within the atom.

In dealing with molecular hydrogen it will be assumed that the effect of the molecular binding is small and that we may represent the scattering to a sufficient approximation by calculating the terms f_0 and

g_0 for the atom, but using the symmetry relations appropriate to a two-electron system.

Before considering the application of the formulae of this section we must first consider in greater detail the approximations involved.

Referring to Chap. VIII, § 4.1, we see that the wave function Ψ must satisfy the orthogonality relations

$$\int \{\Psi - F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\}\psi_0^*(\mathbf{r}_2) \, d\tau_2 = 0$$

$$\int \{\Psi - G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)\}\psi_0^*(\mathbf{r}_1) \, d\tau_1 = 0. \tag{21}$$

The approximate expressions for Ψ do not satisfy these conditions, and consequently terms appear in the expressions for the scattered amplitudes which would vanish if exact formulae could be obtained. Thus in expressions (18), (19), and (20) the terms in $1/r_1$ should vanish. For sufficiently high velocities of impact these terms will be small; but for low velocities the errors introduced will be considerable. However, one cannot simply drop the terms in $1/r_1$ in the amplitude integrals, as the contribution from the remaining terms would also be different in an exact theory. In the absence of a better method it is advisable to retain the terms in $1/r_1$ as partially correcting for the inaccuracy in the remaining terms. Feenberg† has introduced a second method of attempting to correct for the non-orthogonality which may be more accurate. In this method, instead of substituting some such expression as $\mathfrak{F}_0(\mathbf{r}_2)$ for $F_0(\mathbf{r}_2) - G_0(\mathbf{r}_2)$ in (17), he takes

$$\mathfrak{F}_0(\mathbf{r}_2) - \psi_0(\mathbf{r}_2) \int \mathfrak{F}_0(\mathbf{r})\psi_0^*(\mathbf{r}) \, d\tau,$$

which is orthogonal to $\psi_0(\mathbf{r}_2)$. On substituting in (17) we obtain the equations (18) and (19) but with $\int \dfrac{1}{r_{12}} |\psi_0(\mathbf{r}_2)|^2 \, d\tau_2$ in place of $1/r_1$. This method is partially justified by the fact that, if $F_0(\mathbf{r}_1) \pm G_0(\mathbf{r}_1)$ is a solution of the equation (12), then so also is $F_0(\mathbf{r}_1) \pm G_0(\mathbf{r}_1) + c\psi_0(\mathbf{r}_1)$.

The approximation of neglecting the effect of the inelastically scattered waves is connected with the difficulty discussed above; but it will be serious at low velocities in other ways. No satisfactory theory has yet been developed to include the interaction of inelastically scattered waves, but a more accurate method of procedure would probably be to use the method of perturbed stationary state wave functions of Chap. VIII, § 3.3.

† *Phys. Rev.*, **40** (1932), 40, and **42** (1932), 17. See also Morse, *Reviews of Modern Physics*, **4** (1932), 577.

9. Results of Calculation and Comparison with Experiment

The evaluation of the exchange amplitudes for hydrogen and helium has been carried out by Massey and Mohr,[†] using the formulae (18), (19), and (20). For the detailed calculations the reader is referred to the original papers. The chief feature of the exchange terms is that they fall off much faster with increase of velocity of impact than those corresponding to direct scattering. Thus the effect is quite negligible for electrons with energies greater than 70 volts in hydrogen and helium. In order to discuss the effect at low velocities we expand the exchange amplitude in a series of harmonics in the form

$$g(\theta) = \sum (e_{rs} + ie_{is}) P_s(\cos\theta). \tag{22}$$

The convergence of this series is very similar to that of the corresponding series for the directly scattered waves, which we write in the form

$$f(\theta) = \sum_s (d_{rs} + id_{is}) P_s(\cos\theta). \tag{23}$$

The scattered amplitude will then be of the form

$$f(\theta) - g(\theta) = \sum_s [(d_{rs} - e_{rs}) + i(d_{is} - e_{is})] P_s(\cos\theta). \tag{24}$$

For low velocities of impact it was pointed out in § 6 that only the terms d_{r0}, d_{i0} are important in f_0, and so the resulting scattering would be independent of angle for voltages less than 15 volts in helium, and 20 volts in hydrogen. This is in contradiction with experiment; we are now in a position to see that the introduction of exchange is capable of removing this difficulty. For high velocities of impact (greater than 100 volts) the e_{rs}, e_{is} are all negligible; as the velocity decreases, the amplitudes e_{r0}, e_{i0} increase rapidly, and as they are of the same sign as d_{r0}, d_{i0}, this results in a considerable decrease in the zero-order term in (24). The first harmonic thus becomes appreciable, and the angular distribution non-uniform, as observed experimentally.

The exact evaluation of the exchange effect is very difficult, the formulae (18), (19), (20) not being very accurate. Using these formulae Massey and Mohr[‡] have, however, shown that marked deviations from uniformity should occur at voltages below 15 volts in helium and 5 volts in hydrogen, in agreement with experiment (cf. Fig. 22). It was also shown that the formulae are capable of giving the general form of the experimental curves.

However, the formulae (18), (19), (20) predict too complete an inter-

[†] *Proc. Roy. Soc.*, A, **132** (1931), 605; **136** (1931), 289; and **139** (1932), 187.
[‡] Ibid. **136** (1931), 289, and **139** (1932), 187.

ference of the two waves, resulting in the existence of a pronounced minimum in the theoretical cross-section velocity curves for both helium and hydrogen. This has been observed to a modified extent in hydrogen by Normand,[†] but not in helium. The curves are extremely sensitive to the phase factors η_s, and the appearance of the same phase factors in both direct and exchange amplitudes produces the very strong interference. It is very probable that a small difference in the phase factors would greatly improve the theory.[‡]

It is not quite clear at the time of writing why electron exchange is not more important in the scattering of electrons by heavy atoms. The close agreement obtained by use of Faxén and Holtsmark's method would seem to indicate that the exchange effect is small in such cases. In this connexion it is of interest to note that Massey and Mohr[§] found that exchange is relatively less important for helium than for hydrogen. It may be a general result that the heavier the atom the less the importance of exchange. It is conceivable also that the agreement obtained by Faxén and Holtsmark's method is not really as complete a test as would be imagined at first sight. The cross-sections and angular distributions are determined by the size of the atoms, and this determines the magnitude and form of both the directly scattered and exchanged waves in much the same way. The experiments of Mohr and Nicoll[||] have shown how important the size of the atom is in determining the diffraction effects. They find that the angular distributions of electrons which have excited the most probable level in mercury and in argon follow very closely the form of the angular distribution of the elastically scattered electrons, provided the energy loss is small compared with the incident energy. The closeness of the agreement will be clear by reference to Fig. 32, Chap. XI. Thus, despite the different nature of the scattering process, the diffraction effects are determined by the wave-length and size of the atom in both cases. It needs no very great extrapolation of these results to make it possible that the effects of exchange and direct elastic scattering are almost indistinguishable for collisions with heavy atoms. However, we must leave this point undecided until more accurate methods of treatment have been evolved. The effect of inelastic collisions must be included and a more accurate solution of the equations (9) obtained, allowing for the perturbation of the atomic field by the incident and outgoing waves.

[†] *Phys. Rev.*, **35** (1930), 1217.
[‡] It is also possible that considerable improvement would be effected by allowing for the effect of polarization (cf. § 10).   [§] Loc. cit.   [||] Loc. cit.

10. The Effect of Polarization

So far we have neglected all consideration of the effect of the inelasti-
cally scattered waves on the elastic scattering. At the time of writing
this effect has not been considered quantitatively, but we may show
that it will result in a more rapid variation of scattering with angle at
small angles of scattering, and may thus be the explanation of the
discrepancies observed at these angles in helium (cf. Chap. IX, § 3.1).

Let us consider for simplicity the scattering of electrons by hydrogen
atoms. Referring to Chap. VIII, § 1, we see that the function $F_0(\mathbf{r}_1)$
describing the elastic scattering satisfies the equation

$$(\nabla^2 + k^2) F_0(\mathbf{r}_1) = \frac{8\pi^2 m}{h^2} \sum_n V_{n0}(\mathbf{r}_1) F_n(\mathbf{r}_1), \tag{25}$$

where

$$V_{0n} = \epsilon^2 \int \left(\frac{1}{r_{12}} - \frac{1}{r_1} \right) \psi_0(\mathbf{r}_2) \psi_n^*(\mathbf{r}_2) \, d\tau_2.$$

It was also shown that, within the accuracy of Born's first approxima-
tion,

$$F_n(\mathbf{r}_1) = -\frac{2\pi m}{h^2} \int \frac{\exp\{ik_n|\mathbf{r}_1 - \mathbf{r}_3|\}}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_3) V_{0n}(\mathbf{r}_3) \, d\tau_3. \tag{26}$$

We now make the assumption that the velocity of the incident electrons
is so high that $k_n \simeq k$ for all waves $F_n(\mathbf{r}_1)$ of appreciable amplitude.
With this assumption we obtain, on substitution in (25), the formula

$$(\nabla^2 + k^2) F_0(\mathbf{r}_1)$$

$$= -\frac{16\pi^3 m^2}{h^4} \int \frac{\exp\{ik|\mathbf{r}_1 - \mathbf{r}_3|\}}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_3) \sum_n V_{n0}(\mathbf{r}_1) V_{0n}(\mathbf{r}_3) \, d\tau_3. \tag{27}$$

Now

$$\sum_n V_{n0}(\mathbf{r}_1) V_{0n}(\mathbf{r}_3) = \int V(\mathbf{r}_2, \mathbf{r}_3) V(\mathbf{r}_2, \mathbf{r}_1) |\psi_0(\mathbf{r}_2)|^2 \, d\tau_2, \tag{28}$$

where

$$V(\mathbf{r}_2, \mathbf{r}_3) = \epsilon^2 \left(\frac{1}{r_{23}} - \frac{1}{r_3} \right). \tag{29}$$

We thus obtain finally

$$(\nabla^2 + k^2) F_0(\mathbf{r}_1) = -\frac{16\pi^3 m^2}{h^4} \times$$

$$\times \int \int \frac{\exp\{ik|\mathbf{r}_1 - \mathbf{r}_3|\}}{|\mathbf{r}_1 - \mathbf{r}_3|} \exp(ik\mathbf{n}_0 \cdot \mathbf{r}_3) V(\mathbf{r}_2, \mathbf{r}_3) V(\mathbf{r}_2, \mathbf{r}_1) |\psi_0(\mathbf{r}_2)|^2 \, d\tau_2 \, d\tau_3. \tag{30}$$

The evaluation of this integral is extremely laborious for the high
velocities at which it represents a good approximation, but we may

obtain an idea of the effect which it will have on the scattering as follows:

For sufficiently high velocities the main contribution to the integral in (30) will arise from values of the vector $\mathbf{r}_3$ in the neighbourhood of $\mathbf{r}_1$. We may then write approximately, for the right-hand side of (30),

$$-\frac{16\pi^3 m^2}{h^4}\exp(ik\mathbf{n}_0\cdot\mathbf{r}_1)\int\int [V(\mathbf{r}_2,\mathbf{r}_3)]^2\frac{\exp\{ik|\mathbf{r}_1-\mathbf{r}_3|\}}{|\mathbf{r}_1-\mathbf{r}_3|}|\psi_0(\mathbf{r}_2)|^2\,d\tau_2 d\tau_3. \quad (31)$$

To this approximation we may treat these terms as giving rise to an additional potential

$$V' = \frac{2\pi m}{h^2}\int\int [V(\mathbf{r}_2,\mathbf{r}_3)]^2\frac{\exp\{ik|\mathbf{r}_1-\mathbf{r}_3|\}}{|\mathbf{r}_1-\mathbf{r}_3|}|\psi_0(\mathbf{r}_2)|^2\,d\tau_2 d\tau_3. \quad (32)$$

Writing $$\int [V(\mathbf{r}_2,\mathbf{r}_3)]^2|\psi_0(\mathbf{r}_2)|^2\,d\tau_2 = \{V^2(\mathbf{r}_3)\}_{00},$$

we have $$V' = \frac{2\pi m}{h^2}\int \{V^2(\mathbf{r}_3)\}_{00}\frac{\exp\{ik|\mathbf{r}_1-\mathbf{r}_3|\}}{|\mathbf{r}_1-\mathbf{r}_3|}\,d\tau_3. \quad (33)$$

In this calculation we have included the terms due to the elastic scattering on the right-hand side of (25); thus to obtain the polarization potential we must subtract the contribution from these terms. This may be easily shown to lead to the following final form for the polarization potential

$$V_P \simeq \frac{2\pi m}{h^2}\int [\{V^2(\mathbf{r}_3)\}_{00}-\{V_{00}(\mathbf{r}_3)\}^2]\frac{\exp\{ik|\mathbf{r}_1-\mathbf{r}_3|\}}{|\mathbf{r}_1-\mathbf{r}_3|}\,d\tau_3. \quad (34)$$

Referring to the form (29) for $V(\mathbf{r}_2,\mathbf{r}_3)$, we see that this potential will have the asymptotic form

$$V_P \sim -Cr_1^{-4},$$

which is to be contrasted with the form of the undisturbed atomic potential, namely, $$V_{00} \sim -Ce^{-\lambda r_1}.$$

As a consequence of the comparative slowness of the variation of V_P with distance at large distances, the convergence of the series of scattered amplitudes of various orders due to this field will be very slow. Although each amplitude may be small, a large number of spherical harmonics will be required to represent the scattering. These harmonics will interfere very strongly at large angles of scattering, but will cohere to give a large amplitude at small angles. This will result in a more marked decrease of scattered intensity at small angles, in quantitative agreement with the experimental evidence (cf. Chap. IX, § 3.1).

The integration of (33) may be carried out without great difficulty;

it is then found that the effect begins to be important at about the correct velocity in helium, but, in view of the approximate nature of the method, exact agreement is not to be expected.

Similar results were obtained by Distel† using the second approximation in Dirac's Method of Variation of Parameters. He found that the scattering due to polarization falls off as $\mathrm{cosec}^{12}\frac{1}{2}\theta$ at large angles, whereas that due to the undisturbed atom falls off as $\mathrm{cosec}^{4}\frac{1}{2}\theta$ only.

For low velocities of impact the only method which may be used to introduce a polarization correction is that described in Chap. VIII, § 3.3, as the Method of Perturbed Stationary State Wave Functions. By using the formulae (55) of Chap. VIII, it may be shown that the polarization field has again the asymptotic form (34) and will result in producing excess scattering at small angles. Referring to Fig. 21, we notice that the curves calculated by Holtsmark's method all predict too small a scattering at small angles (less than 30°), and it seems that this must be due to the neglect of the effect of the polarization.

† *Zeits. f. Physik,* **74** (1932), 785.

XI

INELASTIC COLLISIONS OF ELECTRONS WITH ATOMS

WE limit ourselves in this chapter, except where otherwise stated, to the case of fast electrons $(v \gg \epsilon^2/h)$; the first Born approximation is then sufficient. This introduces sufficient simplification to enable the calculation of the stopping-power of any material, the probability of ionization of an inner level of an atom, etc., to be carried out with sufficient accuracy to make possible a comparison with experiment. We shall first consider in some detail the case of inelastic collisions with hydrogen and helium atoms. It will then be found possible to generalize the results obtained for these simple cases to more complicated atoms.

1. General Formulae

Consider the collision of an electron with an atom in which the atom is raised from the state m to state n by the impact. If E_m, E_n are the energies of the two atomic states and v, v_{mn} the initial and final velocities of the colliding electron, we have

$$\tfrac{1}{2}m(v^2-v_{mn}^2) = E_n-E_m. \tag{1}$$

It was shown in Chapter VIII that, within the range of validity of the first approximation of Born's theory, the differential cross-section corresponding to the collision is given by

$I_{mn}(\theta)\, d\omega$

$$\frac{4\pi^2 m^2}{h^4}\frac{k_{mn}}{k}\Big|\ \Big|\ V(\mathbf{r};\mathbf{R})\exp\{i(k_{mn}\mathbf{n_1}-k\mathbf{n_0})\cdot\mathbf{R}\}\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\, d\mathbf{r}d\mathbf{R}\ \ d\omega, \tag{2}$$

where $kh\mathbf{n_0}/2\pi$, $k_{mn}h\mathbf{n_1}/2\pi$ are the initial and final momentum vectors of the colliding electron, and ψ_m, ψ_n are the initial and final atomic wave functions of the atom. The interaction energy V is the Coulomb interaction between the incident and atomic electrons, $\epsilon^2/|\mathbf{r}-\mathbf{R}|$.†

We note that the probability of a transition from one state to another of a different term system (such as a singlet-triplet transition in helium) is zero to this approximation, since the perturbing potential V is symmetrical in the coordinates of the atomic electrons, whereas the wave functions ψ_n, ψ_m will have different symmetry properties. The integral in (2) will therefore vanish. This result is in agreement with experiment for fast collisions, but not for slow collisions. The discrepancy

† The effect of the Coulomb interaction between the incident electron and the atomic nucleus vanishes on account of the orthogonal properties of the atomic wave functions.

is due to neglect of electron exchange, as is explained in § 5 of this chapter.

If the colliding electron ionizes the atom, the state n will lie in the continuous spectrum. We distinguish a level of the continuous spectrum by a quantity κ related to the energy of the level by the formula

$$E_\kappa = \kappa^2 \hbar^2 / 8\pi^2 m. \tag{3}$$

The normalization of continuous wave functions is discussed in Chap. XIV, § 2.3. We normalize in such a way that the differential cross-section given by (2), multiplied by $d\kappa$, corresponds to a range of energy such that κ lies between κ and $\kappa + d\kappa$; we must thus have

$$\int_0^\infty \psi_\kappa(\mathbf{r})\psi_{\kappa'}(\mathbf{r})\, d\mathbf{r} = \delta(\kappa - \kappa'). \tag{4}$$

The differential cross-section corresponding to the excitation of a set of continuous energy-levels lying between κ and $\kappa + d\kappa$ is then given by

$$I_{m\kappa}(\theta)\, d\kappa = \frac{4\pi^2 m^2}{\hbar^4} \frac{k_{m\kappa}}{k} \Big| \int\int V \exp\{i(k_{m\kappa}\mathbf{n_1} - k\mathbf{n_0})\cdot\mathbf{R}\}\psi_\kappa^* \psi_m\, d\mathbf{r} d\mathbf{R}\Big|\ d\kappa. \tag{5}$$

1.1. *Introduction of Momentum Variables.*

For most purposes it is convenient to change from angular to momentum variables. The vector

$$(k_{mn}\mathbf{n_1} - k\mathbf{n_0})\hbar/2\pi$$

is the change of momentum of the incident electron. If we choose the axis of a system of polar coordinates along this vector, we have†

$$\exp\{i(k_{mn}\mathbf{n_1} - k\mathbf{n_0})\cdot\mathbf{R}\} = \exp(iKX), \tag{6}$$

where

$$K = |k_{mn}\mathbf{n_1} - k\mathbf{n_0}|$$
$$= (k_{mn}^2 + k^2 - 2kk_{mn}\cos\theta)^{\frac{1}{2}}. \tag{7}$$

The scalar K denotes the magnitude of the momentum change when an electron is scattered through an angle θ. Since

$$K\, dK = kk_{mn}\sin\theta\, d\theta,$$

we have, for the cross-section for momentum change between K and $K + dK$,

$$I_{mn}(K)\, dK = \frac{8\pi^3 m^2}{\hbar^4} \frac{dK}{Kk^2} \Big| \int\int V e^{iKX}\psi_m \psi_n^*\, d\mathbf{r} d\mathbf{R}\Big|^2. \tag{8}$$

This expression for $I_{mn}(K)$ may be simplified by performing the integration over the coordinates of the colliding electron. Let the Z atomic

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† Compare Chap. VII, § 1. We write X in place of Z to avoid confusion with the effective nuclear charge Z.

electrons be denoted by suffixes $1, 2, \ldots, Z$. Then

$$\int V e^{iKX} \, d\mathbf{R} = \epsilon^2 \sum_{s=1}^{s=Z} \int \frac{e^{iKX}}{|\mathbf{R} - \mathbf{r}_s|} \, d\mathbf{R}.$$

Making use of the formula†

$$\int \frac{\exp(iK\mathbf{n}\cdot\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' = \frac{4\pi}{K^2} e^{iK\mathbf{n}\cdot\mathbf{r}},$$

we have

$$\int V e^{iKX} \, d\mathbf{R} = \frac{4\pi\epsilon^2}{K^2} \sum_{s=1}^{s=Z} e^{iKx_s}. \tag{9}$$

Substituting in (8), we then obtain finally

$$I_{mn}(K) \, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} |\epsilon_{mn}(K)|^2, \tag{10}$$

where

$$\epsilon_{mn}(K) = \sum_{s=1}^{s=Z} \int e^{iKx_s} \psi_m \psi_n^* \, d\mathbf{r}. \tag{11}$$

The effective cross-section corresponding to the mn transition will be obtained by integrating the differential cross-section (10) between the limits of allowed momentum change, i.e.

$$Q_{mn}(k) = \int_{K_{\min}}^{K_{\max}} I_{mn}(K) \, dK. \tag{12}$$

In view of their importance in the following sections we will examine these limits for the particular case of fast electrons. It is easily seen that

$$K_{\max} = k + k_{mn}$$
$$K_{\min} = k - k_{mn},$$

and that, as a consequence of the energetic relation (1),

$$k^2 = k_{mn}^2 + 8\pi^2 m (E_n - E_m)/h^2.$$

For the case of fast collisions we have, then,

$$k_{mn} \simeq k - 4\pi^2 m (E_n - E_m)/kh^2,$$

and so

$$k + k_{mn} \simeq 2k$$
$$k - k_{mn} \simeq 4\pi^2 m (E_n - E_m)/h^2 k. \tag{13}$$

2. Calculation of Differential Cross-sections for Hydrogen and Helium. Angular Distributions of Inelastically Scattered Electrons

2.1. *Excitation of Discrete Levels.*

To calculate the differential cross-section $I_{mn}(K) \, dK$ we require the wave functions of the states m, n. In all cases we suppose the initial

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† Bethe, *Ann. der Phys.*, 5 (1930), 325.

level to be the ground state, for which we use the suffix 0. Also we write k_n for k_{0n}. The wave functions for the ground states† are

$$\psi_0 = (\pi a_0^3)^{-\frac{1}{2}} e^{-r_1/a_0} \qquad \text{for hydrogen,}$$
$$= Z^3 (\pi a_0^3)^{-1} e^{-Z(r_1+r_2)/a_0} \qquad \text{for helium, with } Z = 1 \cdot 69. \qquad (14)$$

For the higher states of hydrogen-like atoms the wave functions ψ_{nlm} take the form‡

$$\psi_{nlm} = N_{nlm} r_1^l \, L_{n+l}^{2l+1}\left(\frac{2r_1 Z}{na_0}\right) \exp\left(-\frac{Zr_1}{na_0}\right) P_l^m(\cos\theta_1) e^{\pm im\phi_1},$$
$$N_{nlm}^2 = \frac{2^{2l}}{n\pi}(2l+1)\frac{(l-m)!(n-l-1)!}{(l+m)!\{(n+l)!\}^3}\left(\frac{Z}{na_0}\right)^{2l+3}, \qquad (15)$$

where Z is the nuclear charge; for helium it is necessary to make certain approximations, as in the case of the ground state. It has been shown by Eckart§ that a good approximation to the wave function of an excited state of helium (other than an S state) is obtained by taking a symmetrical combination of the product of two wave functions, one representing the ground state of an electron in the field of a charge 2, the other the excited state of an electron in the field of a charge 1.‖ Hence, if we write

$$\psi_{nlm}(Z|r)$$

for the wave function of a single electron in the nlm state in the field of a charge $Z\epsilon$, we may take, as a sufficiently good approximation for the wave function of an excited singlet state of helium, the form

$$2^{-\frac{1}{2}}\{\psi_0(2|r_1)\psi_{nlm}(1|r_2) + \psi_0(2|r_2)\psi_{nlm}(1|r_1)\}, \qquad (16)$$

the two electrons being distinguished by the numerals 1, 2.

On substitution of the wave functions (16), (15), and (14) in the expression (10) for the differential cross-section, we see that

$$\epsilon_{nlm}(K) = \alpha \int \psi_0(Z|r')\psi_{nlm}^*(Z'|r')e^{iKx'}\,d\tau',$$

where

$$\alpha = 1, \qquad Z = Z' = 1 \qquad \text{for hydrogen,}$$
$$\alpha = 2^{\frac{1}{2}}, \qquad Z = 1\cdot 69, Z' = 1 \qquad \text{for helium.}$$

The value of this integral may be calculated†† for all nlm, and we

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† Cf. Chap. IX, § 3.

‡ Sommerfeld, *Introduction to Wave Mechanics*, p. 59.

§ *Phys. Rev.*, **36** (1930), 878.

‖ For S states a more complicated wave function must be used. See Massey and Mohr, *Proc. Roy. Soc.*, A, **140** (1933), 613.

†† Massey and Mohr, *Proc. Roy. Soc.*, A, **132** (1931), 605.

find that

$$\epsilon_{nlm}(K) = 2^{2l+3}n^{l+1}(2l+1)^{\frac{1}{2}}Z^{\frac{5}{2}}(l+1)!\{(n-l-1)!\}^{\frac{1}{2}}\{(n+l)!\}^{-\frac{1}{2}}K^l \times$$

$$\times \frac{\{(nZ-1)^2+4\zeta^2\}^{\frac{1}{2}(n-l-3)}}{\{(nZ+1)^2+4\zeta^2\}^{\frac{1}{2}(n+l+3)}}[(nZ+1)\{(nZ-1)^2+4\zeta^2\}C^{l+2}_{n-l-1}(x) -$$

$$-2nZ\{(nZ-1)^2+4\zeta^2\}^{\frac{1}{2}}\{(nZ+1)^2+4\zeta^2\}^{\frac{1}{2}}C^{l+2}_{n-l-2}(x) +$$

$$+(nZ-1)\{(nZ+1)^2+4\zeta^2\}C^{l+2}_{n-l-3}(x)], \qquad (17)$$

where

$$x = (n^2Z^2-1+4\zeta^2)^{\frac{1}{2}}[\{(nZ+1)^2+4\zeta^2\}\{(nZ-1)^2+4\zeta^2\}]^{-\frac{1}{2}},$$

$$\zeta = \tfrac{1}{2}Kna_0. \qquad (18)$$

The coefficients C^ν_s are defined in terms of the expansion

$$(1-2ut+u^2)^{-\nu} = \sum_{s=0}^{\infty} C^\nu_s(t)u^s.$$

The expressions for these coefficients for $s = 0, 1, 2, 3$ are

$$C^\nu_0(x) = 1, \qquad C^\nu_1(x) = 2\nu x, \qquad C^\nu_2(x) = \nu\{(2\nu+1)x^2-1\},$$

$$C^\nu_3(x) = 2\nu(\nu+1)\{\tfrac{2}{3}(\nu+2)x^3-x\}. \qquad (19)$$

In order to examine the general features of the formulae we will consider the 2 and 3 quantum levels only. In Fig. 25 the angular distributions of electrons of 200 electron volts incident energy scattered after exciting various quantum levels of helium are shown. For purposes of comparison the distributions corresponding to elastic scattering are given. It is clear from these figures that:

(a) The excitation of the optically allowed levels takes place with much greater probability than that of the optically disallowed.

(b) The probability falls off very rapidly with increase in the angle of scattering. At small angles the excitation of the 2^1P level takes place with greater probability than an elastic collision, but the reverse is the case at large angles.

(c) The inelastic scattering is negligible when

$$Ka_0 \gg Z.$$

The reason for this is clearly seen by reference to the formulae (17), (18), (19), which show that, when $Ka_0 \gg Z$, the excitation probability falls off as K^{-12}, K^{-14}, K^{-16} for S, P, D states respectively. Since $Z\epsilon^2/a_0$ is the ionization potential of the atom, we may say that the differential cross-section is negligible when

$$K \gg V_i/\epsilon^2,$$

V_i being the ionization potential of the atom concerned. This result may be generalized immediately for any atom.

In Table I the values of $2\pi I_{0n}(\theta)$ are given, for various velocities of impact and angles of scattering, for a number of inelastic collisions in
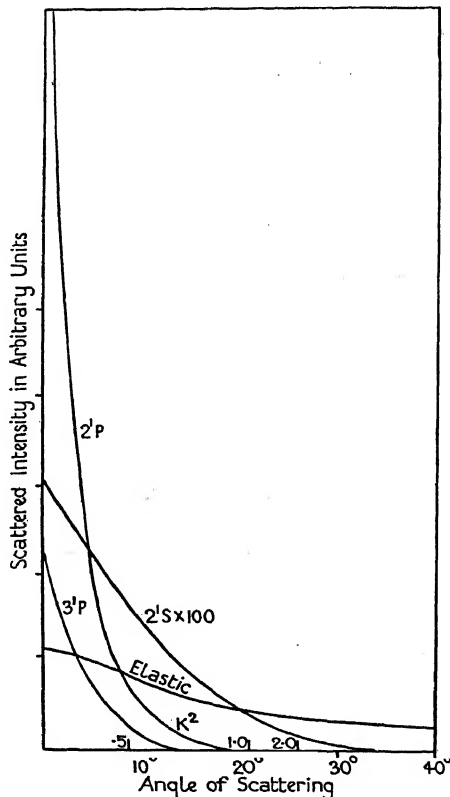
FIG. 25. Angular distribution of electrons of 200 volts incident energy scattered by helium atoms after exciting various levels.
K^2 is given for the 2^1P transition also in atomic units.

helium. It is unlikely, on theoretical grounds, that the formulae obtained by the use of the first approximation of Born's theory can be regarded as very accurate, even for impacts of 200-volt electrons; but comparison with the available experimental material shows that good general agreement is obtained.

Experiments in helium have been carried out by Dymond and

TABLE I

Cross-section $(2\pi I(\theta))$ *in Units of* πa_0^2.

Angle of Scattering.

State Excited.		0°	5°	10°	20°	30°	40°
1¹S	100 volts	0·99	0·98	0·92	0·79	0·61	0·45
	200 ,,	0·99	0·97	0·88	0·65	0·41	0·25
	400 ,,	0·99	0·95	0·77	0·45	0·22	0·10
2¹S	100 volts	0·126	0·120	0·086	0·049	0·020	0·0063
	200 ,,	0·155	0·126	0·086	0·024	0·0039	$0·068_3$
	400 ,,	0·166	0·120	0·057	0·0051	$0·086_3$	$0·03_4$
2¹P	100 volts	7·8	4·4	1·78	0·32	0·056	0·013
	200 ,,	17·7	4·5	0·99	0·068	0·0088	$0·07_3$
	400 ,,	39	2·6	0·33	0·009	0·0003	$0·02_3$
3¹P	100 volts	1·84	1·20	0·45	0·103	0·021	0·0043
	200 ,,	4·5	1·33	0·24	0·027	0·0025	$0·028_3$
	400 ,,	9·7	0·81	0·084	0·0035	$0·014_3$	$0·08_5$
3¹D	100 volts	0·0109	0·0098	0·0070	0·0028	$0·07_3$	$0·014_3$
	200 ,,	0·0132	0·010	0·0052	$0·086_3$	$0·08_4$	$0·07_5$
	400 ,,	0·0142	0·0094	0·0023	$0·011_3$	$0·03_5$	$0·01_6$
4¹P	100 volts	0·68	0·46	0·215	0·043	0·0092	0·0020
	200 ,,	1·71	0·52	0·131	0·011	0·0012	$0·013_3$
	400 ,,	3·7	0·33	0·048	0·0015	$0·06_4$	$0·04_5$

Watson[†] using 200-volt electrons, by McMillen[‡] using 100-volt electrons, and by Mohr and Nicoll[§] using 54-, 83-, 120-, and 196-volt electrons. The observed angular distributions of electrons which have excited the $2P$ level agree well with the theoretical, as may be seen by reference to Fig. 26, in which the comparison is made. For the collisions of the lower velocity electrons (less than 80 volts) the agreement is not good at large angles of scattering, but this failure is to be expected (cf. § 5.2). Comparison of theoretical[||] and observed[††] results for electrons

[†] *Proc. Roy. Soc.*, A, **122** (1929), 571.
[‡] *Phys. Rev.*, **36** (1930), 1034.
[§] *Proc. Roy. Soc.*, A, **138** (1932), 229.
[||] Detailed calculations for atomic hydrogen have been carried out by Elsasser (*Zeits. f. Physik.* **45** (1926) 522), Bethe (*Ann. der Phys.* **5** (1930), 325), and Goldstein (*Thèses*, Paris, (1932)).
[††] Harnwell, *Phys. Rev.*, **34** (1929), 661; Hughes and McMillen, *Phys. Rev.*, **41** (1932), 39; Mohr and Nicoll, *Proc. Roy. Soc.*, A, **138** (1932), 469.

scattered inelastically in hydrogen reveals the same behaviour. (The theory refers to atomic hydrogen, the experiments to the molecule, but at the velocities concerned little difference in behaviour of the two is to be expected, as shown in Chapter XII.)

The observed relative magnitudes of the inelastic and elastic scattering probabilities also agree quite well with the calculated values. It has not yet proved possible to observe electrons which have excited optically
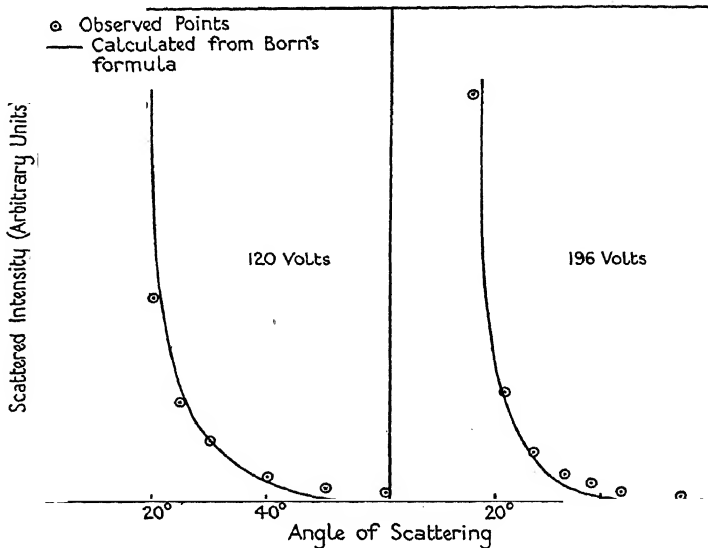
FIG. 26.   Angular distributions of electrons scattered inelastically by helium atoms.

forbidden transitions in helium or hydrogen, which shows that the intensity of such excitation is small. Experiments conducted by Whiddington and Roberts[†] and by van Atta,[‡] in which only non-deviated electrons were examined, exhibit this result very clearly. In Fig. 27 an experimental velocity distribution curve of non-deviated electrons of 200 volts incident velocity through helium is illustrated. Electrons which have excited the 2^1P, 3^1P, and 4^1P levels can be distinguished clearly, but no other inelastically scattered electrons (except those which have made ionizing collisions) can be detected. The relative intensities of excitation of the various P levels is also in good agree-

† *Proc. Leeds Phil. Soc.*, **2** (1931), 201.
‡ *Phys. Rev.*, **38** (1931), 876.

ment with theory. In van Atta's measurements only electrons scattered between angles of 0° and 1° 40′ were collected, and the observed variation of intensity with velocity of electrons which have excited the 2^1P level is in agreement with that given in Table I, a steady increase of intensity with velocity being observed.
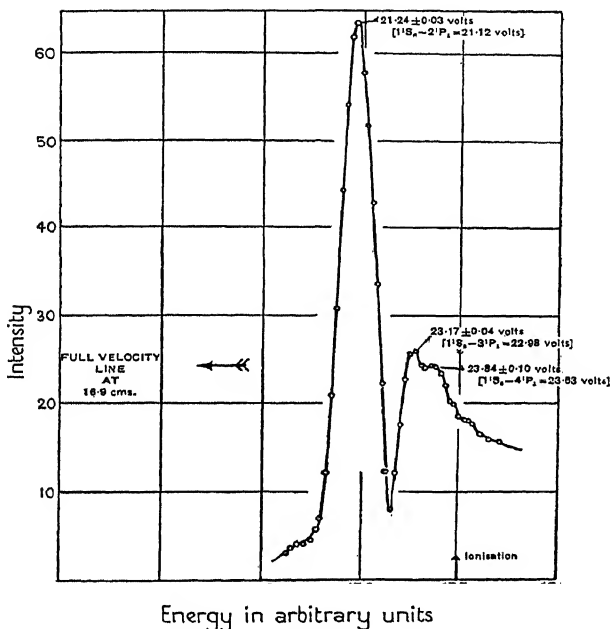
FIG. 27. Velocity analysis of non-deviated electrons of 120 volts incident energy scattered by helium atoms.

We find, then, a close agreement between theory and experiment when this is to be expected. Further comparison with experiment will be discussed in § 3 in connexion with the calculation of total cross-sections. We must now consider the calculation of the differential cross-sections corresponding to the excitation of levels in the continuous spectrum (i.e. to ionization of the atom).

2.2. *Excitation of Continuous Levels. Ionization.*

In any experiment in which ionizing collisions are investigated it is impossible to distinguish between scattered and ejected electrons. If electrons having a definite energy E' are measured after the collision, these will be composed, not only of electrons scattered after losing

energy $E-E'$, but also of electrons ejected from the atom with energy E', E being the energy of the incident electron. In order to compare the results of experiment with observation it is, in general, necessary to allow for the interference of the two sets of electron waves,[†] but under certain conditions this interference may be small and we may apply an approximate theory which does not take account of the interference. For the calculation of the probability of ionization by electrons of a given velocity, the inclusion of interference effects does not alter the result, so we will simply develop the theory without taking such effects into account. We will see later the conditions under which the interference may be neglected in discussing angular and velocity distributions of the electrons.

For hydrogen the wave function corresponding to a state κ of the continuous spectrum in which the electron is moving in the direction with polar angles (χ, ψ) in the field of a charge $Z\epsilon$ is given by[‡]

$$\psi_\kappa^* = \frac{1}{2\pi}\left(\frac{n}{1-e^{-2\pi n}}\right)^{\frac{1}{2}} \frac{e^{i\kappa r}}{\Gamma(1-in)} \int_0^\infty u^{-in}e^{-u}I_0\{2(i\kappa\xi u)^{\frac{1}{2}}\}\,du,$$

where

$$\xi = r(1+\cos\Theta),$$

$$\cos\Theta = \cos\theta\cos\chi + \sin\theta\sin\chi\cos(\phi-\psi),$$

and

$$n = Z/\kappa a_0. \tag{20}$$

For hydrogen we take $Z = 1$ in (20); it is difficult to obtain a satisfactory wave function for helium. A rough approximation is to take the wave function of the excited electron as hydrogenic in form and corresponding to a nuclear charge 1·69 (the effective nuclear charge of the ground state). This function has the merit of being orthogonal to the ground state wave function: in any case the error made will probably not be great for the high velocities of impact for which Born's first approximation is valid.

Using these wave functions in the formula (10), we find for the differential cross-section corresponding to ejection of the atomic electron with energy E_κ in the direction (χ, ψ) relative to the direction of incidence of the exciting electron, into the cone of solid angle $d\sigma$, the incident electron being scattered in the direction (θ, ϕ) into the cone of

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† Cf. Chap. VIII, § 4.3.

‡ Sommerfeld, *Ann. der Physik*, **11** (1931), 257. The normalization is such that ψ_κ^* represents an outgoing plane wave together with an outgoing spherical wave. (Cf. Chap. XIV, § 2.3.)

solid angle $d\omega$, the expression†

$$I_\kappa(\theta,\phi;\chi,\psi)\,d\sigma d\omega d\kappa = C\{K^4 - 2K^3\kappa\cos\delta + (\kappa^2 + \mu^2)\cos^2\delta\}\times$$
$$\times\{\mu^4 + (K^2 - \kappa^2)^2 + 4\mu^2(K^2 + \kappa^2)\}^{-1}\{K^2 - 2\kappa K\cos\delta + (\kappa^2 + \mu^2)\}^{-4}\times$$
$$\times\exp[-2\mu/\kappa\arctan\{2\mu\kappa/(\kappa^2 - K^2 - \mu^2)\}]\,d\sigma d\omega d\kappa, \qquad (21)$$

where δ is the angle between the vector $k\mathbf{n_0} - k_\kappa\mathbf{n_1}$ (the change of momentum of the incident electron) and the direction (χ,ψ), $\mu = Z/a_0$, and C is a constant independent of the angles of ejection and of scattering.

We note that the expression (21) is a maximum when $\delta = 0$, corresponding to the conservation of momentum in the collision between the incident and atomic electrons. To obtain the angular distribution of the ejected electrons it is necessary to integrate (21) over all angles of scattering of the colliding electron. This can only be done numerically. Two typical angular distributions are illustrated in Fig. 28. The maxima are given by the condition

$$k^2 + \kappa^2 - 2k\kappa\cos\chi = k_\kappa^2$$

which corresponds to the conservation of momentum.

The integration over all angles of ejection may be carried out analytically; we obtain

$$I_\kappa(\theta,\phi)\,d\omega d\kappa = \frac{2^{14}\pi^4 m^2 \epsilon^4 k_\kappa\kappa}{h^4 k K^2}\,\frac{\mu^6\{K^2 + \frac{1}{3}(\mu^2 + \kappa^2)\}}{\{\mu^4 + (K^2 - \kappa^2)^2 + 4\mu^2 K\kappa\}^3}\times$$
$$\times\exp\left\{-\frac{2\mu}{\kappa}\arctan\frac{2\mu\kappa}{K^2 - \kappa^2 + \mu^2}\right\}(1 - e^{-2\pi\mu/\kappa})^{-1}\,d\omega d\kappa. \qquad (22)$$

In Fig. 28 two angular distributions of scattered electrons are illustrated, calculated from this formula, while in Fig. 29 a number of curves are given in terms of the change of momentum K as variable. From these curves we note:

(a) For small velocities of ejection of the atomic electron the angular distribution of the scattered electron falls off uniformly with angle, just as for the discrete excitations.

(b) For higher velocities of ejection of the atomic electron the angular distribution has a sharp maximum at the point where

$$K^2 = \kappa^2, \qquad (23)$$

corresponding to the conservation of momentum in the collision between the atomic and incident electron.

(c) The probability falls off rapidly for large values of K.

† Massey and Mohr, *Proc. Roy. Soc.*, A. **140** (1933) 613.

2.21. *Velocity Distribution of Ejected Electrons.*

The velocity distribution of the ejected electrons will be obtained by integrating the expression (22) over all angles of scattering. This may be carried out numerically. In Fig. 30 a number of velocity distributions are illustrated. For ionization by electrons of incident energies greater than 100 volts the probability of ejection rises rapidly to a

A. Scattered Electrons with 176 volts energy
B. Scattered Electrons with 163 volts energy
C. Ejected Electrons with 13·6 volts energy
D. Ejected Electrons with 0·85 volts energy
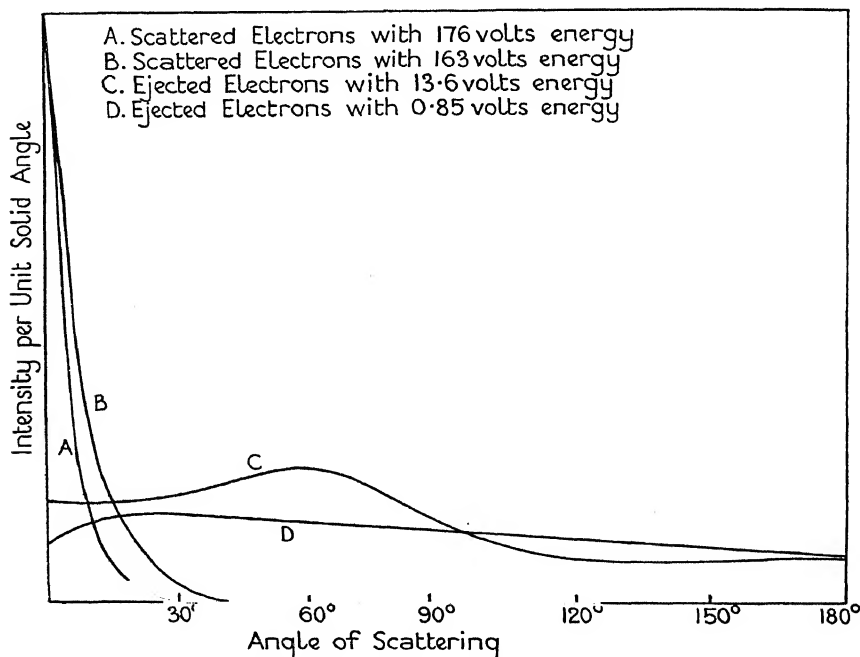
FIG. 28. Angular distributions of scattered and ejected electrons corresponding to electrons of 200 volts incident energy.

maximum for low velocities of ejection and falls off quite rapidly with increasing velocity.

As a consequence of the strong asymmetry of the velocity distribution curve for the ejected electrons, we see that interference should only become important for electrons of intermediate velocity. The general form of the resultant distribution is as shown in the inset of Fig. 30 by the dotted line. The observations of Tate and Palmer† provide a qualitative confirmation of this result.

† *Phys. Rev.*, **40** (1932), 731.
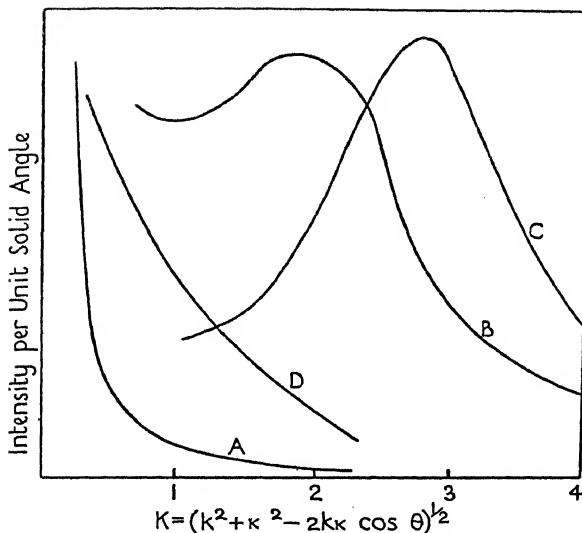
FIG. 29. Angular distribution of electrons scattered after ionizing a helium atom.

	Incident electron.	*Ejected electron.*
A	$k = 4\cdot7$ (300 volts)	$\kappa = 0\cdot5$ (2·5 volts)
B	$k = 4\cdot7$ (300 volts)	$\kappa = 2\cdot0$ (55 volts)
C	$k = 5\cdot9$ (472 volts)	$\kappa = 3\cdot0$ (122 volts)
D	$k = 4\cdot7$ (300 volts)	$\kappa = 1\cdot0$ (14 volts)
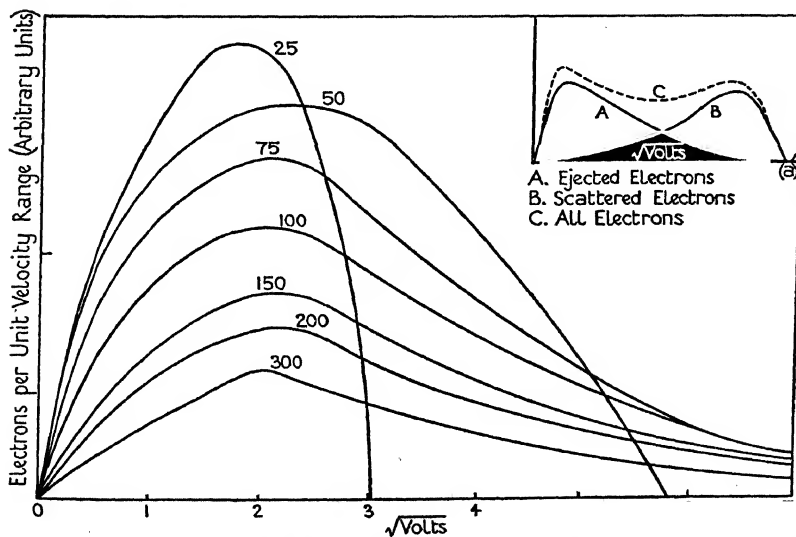
FIG. 30. Velocity distribution of ejected electrons resulting from ionizing collisions with hydrogen atoms.

Numbers denote voltage of incident electrons.

We are now in a position to examine the conditions under which interference may be neglected in discussing the angular distributions. From Fig. 30 it appears that the electrons with low energy should have angular distributions comparable with that calculated from (21) for the ejected electrons, while those with high energy should have angular distributions of the form given by (22) for the scattered electrons. Electrons of intermediate velocity should have angular distributions showing marked interference effects. There is little experimental evidence on this subject, but Tate and Palmer (loc. cit.) have shown that in mercury vapour the angular distribution of the faster electrons resulting from an ionizing collision (the 'scattered' electrons) is very similar to that of electrons resulting from the excitation of discrete levels, i.e. falling off very rapidly with angle of scattering. This is in agreement with the calculated form of curve illustrated in Fig. 28. For the group of slow electrons they find a comparatively small variation of intensity with angle; this would be expected from the form of the curves in Fig. 28 for the ejected electrons when allowance is made for the fact that in the experiments the collected electrons were not homogeneous, but had a voltage range of 30 volts, which would smooth out any maxima which might have appeared. No definite experimental evidence as to interference effects has yet been obtained.

2.3. *Angular Distribution of the Aggregate of Inelastically Scattered Electrons.*

2.31. *Hydrogen Atoms.* Formula (10) gives us the differential cross-section corresponding to a given final state n. If the hydrogen atom is initially in the ground state, we have, summing over all possible states,

$$\sum_{n \neq 0} I_{0n}(K) \, dK = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^2 K^3} \sum_n \left| \int e^{iKx} \psi_0 \psi_n^* \, d\tau \right|^2 dK. \tag{24}$$

Now, if we expand $\psi_0 e^{iKx}$ in a series of atomic wave functions, we obtain

$$e^{iKx} \psi_0 = \sum_{n \neq 0} \psi_n \int e^{iKx} \psi_0 \psi_n^* \, d\tau,$$

and similarly

$$e^{-iKx} \psi_0^* = \sum_{n \neq 0} \psi_n^* \int e^{-iKx} \psi_0^* \psi_n \, d\tau.$$

Multiplying these equations together, we obtain

$$|\psi_0|^2 = \left| \sum_n \psi_n \int e^{iKx} \psi_0 \psi_n^* \, d\tau \right|^2.$$

Integrating both sides of this equation over all space, we obtain, by

virtue of the orthogonal properties of the wave functions ψ_n,

$$1 = \left| \int e^{iKx} |\psi_0|^2 \, d\tau \right|^2 + \sum_n \left| \int e^{iKx} \psi_0 \psi_n^* \, d\tau \right|^2.$$

Substituting in (24) then gives

$$\sum_{n \neq 0} I_{0n}(K) \, dK = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^2} \frac{dK}{K^3} [1 - \{F(K)\}^2], \tag{25}$$

where F is the atomic scattering factor [see Chap. VII, § 1, eq. (9)] for the hydrogen atom, given by

$$F(K) = \int e^{iKx} |\psi_0|^2 \, d\tau.$$
$$= (1 + \tfrac{1}{4} K^2 a_0^2)^{-2}.$$

The condition of validity of this formula is that no appreciable contribution to the sum (24) arises from transitions $0 \to n$ which are not energetically possible. For this to be so, K must be greater than the minimum momentum change for a transition to the highest state with appreciable excitation probability; i.e. if E_κ is the energy of this state, we must have, using the expression (13) for $K_{\min}$,

$$K > 4\pi^2 m (E_\kappa - E_0)/kh^2.$$

The excitation probability falls off rapidly with increasing E_κ and can certainly be taken as small when

$$E_\kappa > -4E_0.$$

The condition of validity of the formula (25) is then roughly that

$$K > 20\pi^2 m |E_0|/kh^2.$$

If the energy of the incident electron is great compared with the excitation energy of the state of the atom excited, we have

$$K^2 = (2k^2 - \lambda_n^2)(1 - \cos\theta) - \frac{1}{4} \frac{\lambda_n^4}{k^2} \cos\theta + \dots,$$

where

$$\lambda_n^2 = \frac{8\pi^2 m}{h^2} (E_n - E_0).$$

For all angles θ which satisfy

$$\theta \gg \frac{\lambda_n^2}{k^2} \tag{26}$$

we have, therefore,

$$K = 2k \sin\tfrac{1}{2}\theta, \qquad k_n \simeq k. \tag{27}$$

This result is independent of n and may be used provided $E \gg E_n - E_0$, i.e. for small angle collisions. For large angle collisions we make use of the fact that the momentum of the secondary electron ejected is

approximately equal to $\dfrac{h}{2\pi} K$, so the energy lost by the incident electron is

$$E_\kappa - E_0 = \frac{8\pi^2 m}{h^2} K^2$$

$$= \frac{8\pi^2 m}{h^2} (k^2 + k_\kappa^2 - 2kk_\kappa \cos\theta).$$

But $$E_\kappa - E_0 = \frac{8\pi^2 m}{h^2} (k^2 - k_\kappa^2),$$

so $$K = k\sin\theta, \qquad k_\kappa = k\cos\theta. \tag{28}$$

These formulae are identical with (27) when θ is small, and so we may use (28) for all θ satisfying (26).

As (28) shows that K and k_κ are independent of the excitation energy, we may immediately convert the sum (25) for a fixed momentum change to a sum at a fixed angle of scattering by using the relation

$$K\,dK = kk_n \sin\theta\,d\theta.$$

in connexion with (28). This gives

$$2\pi \sum_n I_{0n}(\theta)\sin\theta\,d\theta = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^4} \frac{\cos\theta}{\sin^3\theta}\left[1 - \frac{1}{(1+\tfrac{1}{4}k^2 a_0^2 \sin^2\theta)^4}\right]d\theta$$

which is to be compared with formula (9) of Chapter IX for the elastic scattering

$$2\pi I(\theta)\sin\theta\,d\theta = \frac{128\pi^5 m^2 \epsilon^4 a_0^4}{h^4} \frac{(8+4k^2 a_0^2 \sin^2 \tfrac{1}{2}\theta)^2}{(4+4k^2 a_0^2 \sin^2 \tfrac{1}{2}\theta)^4}\sin\theta\,d\theta.$$

For small angles of scattering [but still satisfying (26)] we have

$$\frac{\sum\limits_n I_{0n}(\theta)}{I(\theta)} = \cot\theta. \tag{29}$$

Hence the inelastic scattering at small angles considerably exceeds the elastic.

At large angles

$$2\pi \sum_n I_{0n}(\theta) = \frac{128\pi^5 m^2 \epsilon^4}{h^4 k^4} \operatorname{cosec}^4\theta,$$

which is the Rutherford formula for scattering of one electron by another. We must correct this formula to include the interference of the scattered and ejected electrons. Using the formula (26) of Chapter V when ϵ^2/hv is small we obtain

$$2\pi \sum_n I_{0n}(\theta)\sin\theta\,d\theta = \frac{128\pi^5 m^2 \epsilon^4}{k^4 h^4}\sin\theta\cos\theta(\operatorname{cosec}^4\theta - \operatorname{cosec}^2\theta\sec^2\theta + \sec^4\theta)$$

$$= \frac{64\pi^5 m^2 \epsilon^4}{k^4 h^4}\frac{4-3\sin^2 2\theta}{\sin^2 2\theta}d\theta. \tag{30}$$

This is to be compared with the corresponding formula for the elastic scattering

$$2\pi I(\theta)\sin\theta\,d\theta \sim \frac{16\pi^5 m^2\epsilon^4}{h^4 k^4}\frac{\cos\frac{1}{2}\theta}{\sin^3\frac{1}{2}\theta}\,d\theta.$$

From formulae (29) and (30) we see that inelastic scattering predominates near 0° and 90° but may become smaller than the elastic at intermediate angles.

2.32. *Generalization for Complex Atoms.* In order to obtain approximate results for complicated atoms, we approximate to the wave functions by taking them as sums of products of hydrogen-like wave functions for the single electrons, the sum having the correct symmetry. The results obtained for hydrogen atoms can then be taken over to apply to complex atoms; we must, however, subtract the contributions made by the forbidden transitions from, say, the K-level to an occupied state in the L-level. We consider the probability of a transition from the nl shell of an atom to the $n'l'$ shell. The differential cross-section corresponding to this will be

$$I_{nl,n'l'}(K)\,dK = \frac{128\pi^5 m^2\epsilon^4}{k^2 h^4}\frac{dK}{K^3}|\epsilon_{nl,n'l'}(K)|^2. \tag{31}$$

If there are Z_{nl} electrons in the nl shell, $\overleftarrow{Z}_{nl}$ of which have spins in one direction, $\overrightarrow{Z}_{nl}$ in the other, we have

$$I_{nl,n'l'}(K)\,dK = \frac{128\pi^5 m^2\epsilon^4}{k^2 h^4}\frac{dK}{K^3}\times$$

$$\times\{Z_{nl}|\epsilon_{nl,n'l'}(K)|^2-\text{contribution from excluded transitions}\}. \tag{32}$$

Here $\epsilon'_{nl,n'l'}(K)$ refers to the single electron wave functions and is given by

$$|\epsilon'_{nl,n'l'}(K)|^2 = \frac{1}{2l+1}\sum_{m=-l}^{m=l}\left|\int\psi_{nlm}\psi^*_{n'l'm}e^{iKx}\,d\tau\right|^2 \tag{33}$$

the summation being necessary in order to allow for the degeneracy in the magnetic quantum number. It is now easy to see that, since there can be no reversal of spin in the transition, the contribution from excluded transitions is simply

$$\frac{1}{2l'+1}(\overrightarrow{Z}_{nl}\overrightarrow{Z}_{n'l'}+\overleftarrow{Z}_{nl}\overleftarrow{Z}_{n'l'})|\epsilon'_{nl,n'l'}(K)|^2.$$

If we write
$$Z_{nl}-\frac{1}{2l'+1}(\overrightarrow{Z}_{nl}\overrightarrow{Z}_{n'l'}+\overleftarrow{Z}_{nl}\overleftarrow{Z}_{n'l'}) = \zeta_{nl,n'l'}, \tag{34}$$

we have then

$$I_{nl,n'l'}(K)\, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \zeta_{nl,n'l'} |\epsilon'_{nl,n'l'}(K)|^2. \tag{35}$$

Applying this result to the aggregate of inelastic collisions with a complex atom, we obtain

$$\sum_{nl} \sum_{n'l'} I_{nl,n'l'}(K)\, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \Big\{ Z - 2 \sum_{nl} (2l+1) F_{nl}^2(K) -$$
$$- 2 \sum_{nl} \sum_{n'l'} \sum_m \Big| \int \psi_{nlm} \psi_{n'l'm} e^{iKx}\, d\tau \Big|^2 \Big\}, \tag{36}$$

F_{nl} being the F-factor corresponding to the nl shell. By means of this formula the form of the angular distribution of the aggregate of inelastic collisions may be obtained just as in § 2.31, and similar results are arrived at.

3. Total Collision Cross-sections

3.1. *Excitation of Discrete Optical Levels.*

The total cross-section corresponding to the excitation of the nth quantum state of a given atom from the ground state is given by

$$\int\limits^{K_{max}} I_{0n}(K)\, dK. \tag{37}$$

The limits of integration have been given in equations (13). In order to evaluate this integral approximately, we observe (cf. Fig. 25 and Table 1) that $I_{0n}(K)$ becomes very small for such values of K that

$$K^2 > K_0^2, \tag{38}$$

where
$$K_0^2 = 8\pi^2 m |E_0|/h^2.$$

When this condition is not satisfied we may expand $I_{0n}(K)$ in powers of K. We have, from equation (10),

$$I_{0n}(K)\, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \Big| \int e^{iKx} \psi_0 \psi_n^*\, d\tau \Big|^2.$$

Expanding the exponential, we obtain

$$I_{0n}(K)\, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \{ K^2 |x_{0n}|^2 + \tfrac{1}{4} K^4 |(x^2)_{0n}|^2 + \ldots \}, \tag{39}$$

where x_{0n}, $(x^2)_{0n}, \ldots$ are the matrix elements of $x, x^2, \ldots$, so that

$$(x^s)_{0n} = \int x^s \psi_0 \psi_n^*\, d\tau.$$

The expansion (39) is valid provided the condition (38) is not satisfied.

When (38) is satisfied, $I_{0n}(K)$ is very small and may be neglected. We may then write

$$Q_{0n} \simeq \frac{128\pi^5 m^2 \epsilon^4}{k^2 \hbar^4} \int_{K_{\min}}^{K_0} \{K^{-1}|x_{0n}|^2 + \tfrac{1}{4}K|(x^2)_{0n}|^2 + \ldots\}\, dK.$$

For a transition which is optically allowed the first term will not vanish and will be much the largest for fast electrons. Carrying out the integration and using the approximate expression (13) for $K_{\min}$, we obtain

$$Q_{0n} \simeq \frac{64\pi^5 m^2 \epsilon^4}{k^2 \hbar^4}|x_{0n}|^2 \log \frac{2mv^2}{E_n - E_0}. \tag{40}$$

If the transition considered is associated with a quadrupole moment but no dipole moment, we obtain similarly

$$Q_{0n} \simeq \frac{128\pi^7 m^3 \epsilon^4}{k^2 \hbar^6}|(x^2)_{0n}|^2 |E_0|. \tag{41}$$

We notice, then, that owing to the logarithmic term, the cross-sections corresponding to the excitation of optically allowed levels should fall off more slowly with increasing velocity of impact than those corresponding to optically forbidden transitions. Experimental evidence on this point is very meagre. Some evidence is obtained from the measurement of the excitation functions of various spectral lines. This method has been mentioned in Chapter IX. However, the results of the most recent experiments carried out by Lees[†] and by Thieme[‡] in helium do not indicate any noticeable differences in behaviour between S, P, and D levels with regard to variation of excitation probability with velocity at high velocities.

A further consequence of the formula (40) is that, as the velocity of impact increases, a greater proportion of the collisions are inelastic, since the cross-section for elastic scattering decreases as v^{-2} for high velocities [see Chap. IX, (10)]. This effect is clearly shown in Table IV of this chapter.

In Table II a number of values of excitation cross-sections for helium calculated by exact integration of the expression (18) are given with the elastic cross-section for comparison. The observed values given for the sum of the elastic and discrete excitation cross-sections are obtained by subtracting the observed ionization probabilities (compared with those calculated in § 3.3) measured by Smith,[§] from the total cross-sections measured by Normand.[||] The agreement at 200 volts is

† *Proc. Roy. Soc.*, A, **137** (1932), 173.   ‡ *Zeits. f. Physik*, **78** (1932), 412.
§ *Phys. Rev.*, **36** (1930), 1293. || Ibid. **35** (1930), 1217.

TABLE II

Cross-sections in units of πa_0^2.

Electron Energy in volts.	Elastic.	State Excited.								Sum.	Observed.
		2^1S	2^1P	3^1P	3^1D	4^1P	4^1D	4^1F	5^1P		
100	0·375	0·0084	0·107	0·031	$0·053_3$	0·012	$0·027_5$	0·040	0·0063	0·538	0·67
200	0·205	0·0047	0·069	0·021	$0·028_3$	0·009	$0·015_5$	0·020	0·0046	0·313	0·31
400	0·107	0·0025	0·047	0·013	$0·025_3$	0·006	$0·08_4$	$0·010_5$	0·0034	0·178	—

very satisfactory, but it appears that Born's approximation begins to fail for electrons with energies less than about 150 volts.

The comparison of relative values for the different transitions with the values obtained from optical experiments is discussed in § 5.2 in connexion with the excitation of triplet levels.

3.2. *Excitation of X-rays.*

In collisions with complex atoms an electron may be ejected from an inner shell, with subsequent X-ray emission. It is thus of considerable interest to obtain approximate expressions for the probability of such inner-shell ionization. We require to sum the probabilities of all the possible transitions from the inner shell concerned.

For ionization of the nl level we require, then,

$$\sum_{n'l'} I_{nl,n'l'}(K)\, dK = \frac{128\pi^5 m^2 \epsilon^4}{k^2 h^4} \frac{dK}{K^3} \sum_{n'l'} \zeta_{nl,n'l'} |\epsilon_{nl,n'l'}(K)|^2. \tag{42}$$

The total cross-section corresponding to this ionization, which we denote by Q_{nl}^i, is then given by

$$Q_{nl}^i = \sum_{n'l'} \int_{K_{\min}}^{K_{\max}} I_{nl,n'l'}(K)\, dK, \tag{43}$$

and we may approximate to the value of this integral in the same way as in the preceding section for optical levels. In this way we find

$$Q_{nl}^i \simeq \frac{64\pi^5 m^2 \epsilon^4}{k^2 h^4} \cdot Z_{nl} \left(\bar{x}_{nl}^2 - \sum_{n'l'} |x_{nl,n'l'}|^2 \right) \log\left(\frac{2mv^2}{B_{nl}} \right), \tag{44}$$

where B_{nl} is of the order of the energy of ionization of the nl shell and $\bar{x}_{nl}^2$ is one-third of the mean square radius of the nl shell. For outer shells the terms $\sum_{n'l'} |x_{nl,n'l'}|^2$ are small, and the probability of ionization of the shell is nearly proportional to the mean square radius of the shell, but for inner shells the intensity of forbidden transitions becomes

important. Bethe† has carried out further approximations by assuming the atomic wave functions to be of hydrogen-like form with effective nuclear charge Z_{eff}. With this assumption he finds, for those inner shells from which the most important discrete transitions are forbidden,

$$\bar{x}_{nl}^2 - \sum_{n'l'} |x_{nl,n'l'}|^2 = 0{\cdot}2 - 0{\cdot}6n^2a_0^2/Z_{\mathrm{eff}}^2. \tag{45}$$

As the energy E_{nl} of the nl shell is

$$E_{nl} = -2\pi^2m\epsilon^4Z_{\mathrm{eff}}^2/n^2h^2,$$

we have finally

$$Q_{nl}^i = \frac{2\pi\epsilon^4Z_{nl}}{mv^2|E_{nl}|} b_{nl} \log\left(\frac{2mv^2}{B_{nl}}\right), \tag{46}$$

where b_{nl} is between $0{\cdot}2$ and $0{\cdot}6$ for inner shells, and of the order n^2 for outer shells.

Experimental evidence as to the correctness of the formula (46) is not yet available. All investigations of the variation of the intensity of characteristic X-ray lines with the energy of the bombarding electrons have been carried out with thick targets, and complicated corrections must be applied to reduce the observations to the corresponding values for thin targets. A detailed investigation of these corrections has been carried out by Webster, Clark, and Hansen,‡ who applied their results to the excitation function of the K-lines of silver observed with a thick target. The energy range of the electrons in these observations extends only up to voltages of three times the excitation voltage, and it is not to be expected that formula (46) would be valid. Actually it is found that the experimental curve rises to a maximum more slowly than that calculated from (46) with B_{nl} taken as four times the excitation energy. The Born formula fails in a similar way when applied to optical excitation (see § 5.2).

3.3. *Primary Ionization.*

Using the differential cross-sections $I_{0\kappa}\,d\kappa\,dK$ given in § 2.2 for the excitation of a level of the continuous spectrum, we may calculate (by numerical integration) the total cross-section Q_0^i for ionization, using the formula

$$Q_0^i = \int\limits_0^{\kappa_{\max}} \int\limits_{K_{\min}}^{K_{\max}} I_{0\kappa}(K)\,dK\,d\kappa, \tag{47}$$

where

$$\kappa_{\max}^2 = k^2 - 8\pi^2m|E_0|/h^2.$$

The results of such a calculation are illustrated in Figs. 31 and 32 for the ionization cross-sections of hydrogen and helium.

† *Ann. der Phys.*, **5** (1930), 325.
‡ *Phys. Rev.*, **37** (1931), 115 and **43** (1933), 839.
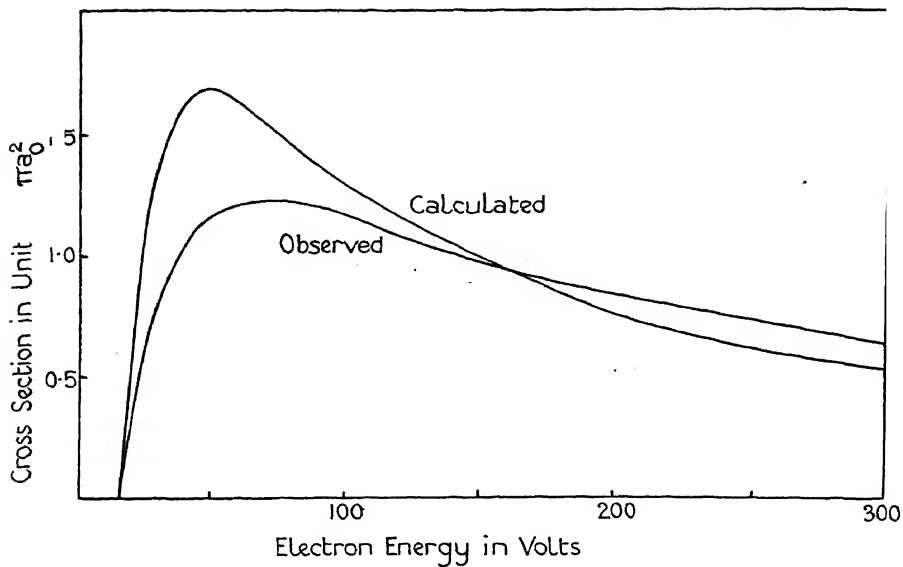
FIG 31. Ionization probabilities in hydrogen.
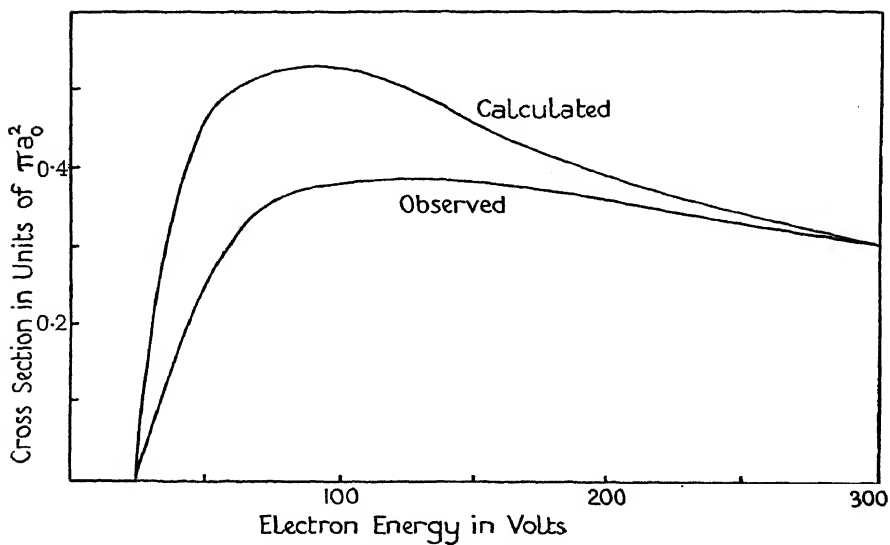
FIG. 32. Ionization probabilities in helium.

The comparison between experimental curves and those calculated is also shown. The most recent experimental measurements have been carried out by P. Smith and Tate† for (molecular) hydrogen and by P. Smith‡ for helium. For purposes of comparison it is assumed that the molecule behaves like two atoms.

The agreement is quite satisfactory when one takes into account the facts that the magnitudes of the cross-sections are compared as well as the variation with velocity, and that it is difficult to obtain approximately correct wave functions to represent ionized states of atoms other than hydrogen. For electrons with energies less than 200 electron volts the theoretical cross-sections are too large, but the disagreement at these low energies of impact is not surprising and will be discussed further in § 5.2. It may be pointed out that the simple theory again predicts too rapid a rise of the probability as the incident energy is increased above the ionization potential, just as for X-ray and optical excitation.

3.31. *Ionization Probability for High-velocity Impacts.*§ Owing to the laborious nature of the calculations for the higher voltage impacts carried out as above, it is important to obtain an approximate formula to cover these cases. In Fig. 30 of this chapter, curves are given which illustrate the dependence of the integral

$$\int_{K_{min}}^{K_{max}} I_{0\kappa}(K)\, dK \tag{48}$$

on κ for various velocities of incidence.

Referring to this figure, we see that the main contribution to the probability of ionization comes from transitions involving quite small values of κ. For such transitions $I_{0\kappa}(K)$ is of the form illustrated in Fig. 29; thus for large values of K it is vanishingly small, just as in the case of the excitation of discrete states. The concentration of the scattered electrons about the angle corresponding to the conservation of momentum occurs only for transitions associated with large values of K. As a consequence we may approximate to the value of Q_0^i in much the same way as for the excitation of discrete states. Using this method, we find

$$Q_{nl}^i = \frac{64\pi^5 m^2 \epsilon^4}{h^4 k^2} Z_{nl} \int d\kappa |x_{nl,\kappa}|^2 \log\left(\frac{2mv^2}{C_{nl}}\right), \tag{49}$$

† *Phys. Rev.*, **39** (1932), 270.   ‡ Ibid. **36** (1930), 1293.
  § By high velocity is understood a velocity greater than 1,000 electron volts but not such a velocity that relativistic effects are important.

where C_{nl} is a quantity of the order of the energy of the shell. Employing methods similar to those used in considering the excitation of X-rays it was shown by Bethe† that (49) reduces to

$$Q_{nl}^i = \frac{2\pi\epsilon^4}{mv^2} \frac{c_{nl}}{|E_{nl}|} Z_{nl} \log\left(\frac{2mv^2}{C_{nl}}\right), \tag{50}$$

where
$$\upsilon_{nl} = (Z_{\text{eff}}^2 \qquad |x_{nl,\kappa}|^2 \, d\kappa.$$

Using again the approximation of hydrogen-like wave functions, the following are the values of c_{nl} for the various shells.

TABLE III

Shell	1s	2s	2p	3s	3p	3d		4p	4d	4f
	0·28	0·21	0·13	0·17	0·14	0·07	0·15	0·13	0·09	0·04

These figures show that shells with the highest azimuthal quantum numbers are the most difficult to ionize.

For hydrogen in particular, for which exact calculation may be carried out,‡ we have for the cross-section for ionization.

$$Q_0^i = 0\cdot285 \, \frac{2\pi\epsilon^4}{|E_0|mv^2} \log\left(\frac{2mv^2}{0\cdot048|E_0|}\right), \tag{51}$$

showing that C_{nl} is about one-tenth of the energy of ionization of the nl shell.

3.32. *Comparison with Classical Theory and with Experiment.* The classical formula of J. J. Thomson§ is of a somewhat different form from (50), as it contains no logarithmic term. The formula is

$$Q_0^i = \frac{2\pi\epsilon^4}{mv^2} \frac{Z_{nl}}{|E_{nl}|}. \tag{52}$$

The very different form of the classical and quantum theoretical expressions makes a comparison with experiment of especial interest. The best substance to choose for the comparison is hydrogen; the use of approximate wave functions is here least likely to lead to serious error, it being unlikely that any important difference between the molecule and atom exists, except the ionization potential which we must take to be that of the molecule (16 volts). The observations of Williams and Terroux‖ for $v = 0\cdot54c$ give the number of ions produced per cm. path at N.T.P. as 12·6. The formula (51) gives 14·7, and the classical formula (52) 3·5. The quantum theory formula thus gives much better agreement.

† *Ann. der Phys.*, **5** (1930), 325.   ‡ Bethe, loc. cit.
§ *Phil. Mag.*, **23** (1912), 449.   ‖ *Proc. Roy. Soc.*, A, **126** (1930), 289.

3.4. *Distribution of Various Types of Collisions for High-velocity Impacts.*

In Table IV† the relative probabilities of different types of collision of high-velocity electrons with hydrogen atoms are given. These values include all relativistic corrections (see Chap. XV, § 2).

TABLE IV

Type of Collision.	Energy of Incident Electron in Volts.					
	1,000	10,000	100,000	10^6	10^8	10^{10}
	Percentage of all Collisions.					
Elastic	8·7	6·5	5·1	4·1	2·55	1·8
Excitation of 2-quantum levels	42·8	45·3	47·5	49·5	51·5	52·8
,, ,, 3- ,, ,,	6·3	7·0	7·3	7·8	8·1	8·4
,, ,, 4- ,, ,,	2·41	2·60	2·71	2·79	2·90	2·96
,, ,, 5- ,, ,,	1·17	.1·24	1·28	1·32	1·36	1·38
,, ,, higher ,, ,,	2·17	2·28	2·33	2·38	2·42	2·45
All discrete levels	54·8	58·4	61·2	63·4	66·4	68·0
Ionization	36·5	35·1	33·7	32·5	31·0	30·2
Energy-loss per primary ion in volts	51·4	59·9	64·8	66·9	68·6	69·4
,, ,, collision ,, ,,	18·7	21·0	21·7	21·7	21·3	21·0
Total cross-section by 10^{-20} cm.	3,200	426	66·0	30·6	42·8	60·0

4. Calculation of the Stopping-power of Matter for Fast Electrons

4.1. *Preliminary Theorems.*

4.11. *Generalized Transition Probabilities and Oscillator Strengths.* It will be found convenient in the calculation of the total energy loss per cm. path of electrons in passing through matter to define certain quantities associated with the various transitions. These quantities are generalizations of quantities associated with optical transitions.

The optical transition probability associated with a transition from the mth to the nth level is defined as

$$\phi_{mn} = 16\pi^4 m^2 \epsilon^4 |x_{mn}|^2 / h^4. \tag{53}$$

We generalize this quantity by writing

$$\phi_{mn}(K) = \frac{16\pi^4 m^2 \epsilon^4}{h^4 K^2} |\epsilon_{mn}(K)|^2,$$

which reduces to (53) for zero momentum change. Associated with the optical transition probability $\phi_{mn}(0)$ is the oscillator strength f_{mn}, which is defined as

$$f_{mn} = R^{-1} \nu_{mn} \phi_{mn},$$

where R is Rydberg's constant and ν_{mn} is the frequency associated with the transition. The generalized oscillator strength associated with the

† Due to Bethe, *Handbuch der Physik*, 2nd edition, xxiv/1 (1933), 519.

$m \to n$ transition is then defined as†

$$f_{mn}(K) = (E_m - E_n)\frac{8\pi^2 m}{K^2 h^2}|\epsilon_{nm}(K)|^2.$$

We note that the differential cross-section corresponding to the $0 \to n$ transition is given by

$$I_{0n}(K)\,dK = \frac{16\pi^3 m\epsilon^4}{k^2 h^2}\frac{1}{E_0 - E_n}f_{0n}(K)\frac{dK}{K}.$$

The loss of energy per cm. path in passing through a gas containing N atoms per c.c. will thus be [cf. equation (60)]

$$-\frac{dT}{dx} = \frac{16\pi^3 m\epsilon^4 N}{k^2 h^2}\sum_n \int_{K_{\min}}^{K_{\max}} f_{0n}(K)\frac{dK}{K}. \tag{54}$$

4.12. *Summation Theorem for Generalized Oscillator Strengths.*

(a) *Hydrogen-like atoms.* Let us consider the value of

$$\sum_n f_{0n}(K) = \frac{8\pi^2 m}{K^2 h^2}\sum_n (E_0 - E_n)\left|\int e^{iKx}\psi_0\psi_n^*\,d\tau\right|^2.$$

The functions ψ_0, ψ_n^* satisfy the equations

$$\nabla^2\psi_0 + \frac{8\pi^2 m}{h^2}(E_0 - V)\psi_0 = 0, \tag{55.1}$$

$$\nabla^2\psi_n^* + \frac{8\pi^2 m}{h^2}(E_n - V)\psi_n^* = 0. \tag{55.2}$$

Multiplying (55.1) by ψ_n^* and (55.2) by ψ_0, subtracting, and integrating over all space, we obtain

$$(E_0 - E_n)\int e^{iKx}\psi_0\psi_n^*\,d\tau = \frac{h^2}{8\pi^2 m}\int (\psi_0\nabla^2\psi_n^* - \psi_n^*\nabla^2\psi_0)e^{iKx}\,d\tau.$$

The right-hand side reduces to

$$\frac{h^2}{8\pi^2 m}\left\{-2iK\int \frac{\partial\psi_0}{\partial x}\psi_n^* e^{iKx}\,d\tau + K^2\int \psi_0\psi_n^* e^{iKx}\,d\tau\right\}. \tag{56}$$

Now

$$\sum_n \left[\int \frac{\partial\psi_n}{\partial x}\psi_0^* e^{iKx}\,d\tau\right]\left[\int \psi_n\psi_0^* e^{-iKx}\,d\tau\right] = \int \frac{\partial\psi_0}{\partial x}\psi_0^*\,d\tau = 0,$$

as may be proved by following a method similar to that used in § 2.3.

† Bethe, *Ann. der Phys.*, 5 (1930), 325.

We then have

$$\frac{8\pi^2 m}{K^2 h^2} \sum_n (E_0 - E_n) \left| \int e^{iKx} \psi_0 \psi_n^* \, d\tau \right|^2 = \sum \left| \int \psi_n \psi_0^* e^{iKx} \, d\tau \right|^2$$

$$= \left| \int |\psi_0|^2 \, d\tau \right| = 1.$$

Hence finally we see that

$$\sum f_{0n}(K) = 1. \tag{57}$$

(b) *Complex atoms.* As a generalization of the formula we require the sum of the oscillator strengths from a particular shell of a given atom. Making use as before of hydrogenic wave functions, the only modification required in the treatment above is to allow for the oscillator strengths of forbidden transitions (transitions to levels already filled). We then find for the sum of the oscillator strengths from the nl shell

$$f_{nl} = \sum_{n'l'} f_{nl,n'l'} = Z_{nl} - \sum_{n'l'} \frac{\overrightarrow{Z}_{nl} \overrightarrow{Z}_{n'l'} + \overleftarrow{Z}_{nl} \overleftarrow{Z}_{n'l'}}{2l'+1} f'_{nl,n'l'}, \tag{58}$$

where $f'_{nl,n'l'}$ is the oscillator strength of a single electron transition from the nl to the $n'l'$ level. The second term in (58) is the sum of the oscillator strengths of the forbidden transition. In particular, if all shells $n''l''$ are filled,

$$\overrightarrow{Z}_{n''l''} = \overleftarrow{Z}_{n''l''} = 2l''+1,$$

and so

$$f_{nl} = Z_{nl}\Big(1 - \sum_{n''l''} f'_{nl,n''l''}\Big). \tag{59}$$

It is of interest to note that

$$\sum_{nl} f_{nl} = Z,$$

as may readily be shown. The sum of the oscillator strengths for the inner shells of a complex atom is less than the number of electrons in the shell; for outer shells it is greater.

Using hydrogenic wave functions Bethe[†] has compiled a table of approximate oscillator strengths associated with the shells of various atoms of the periodic table. Table V is a reproduction of this.

4.2. *Calculation of the Stopping-power.*

4.21. *Hydrogen.* The loss of energy per cm. path, $-dT/dx$, of an electron passing through a gas containing N atoms per c.c. is given by

$$-\frac{dT}{dx} = N \sum_n \int_{K_{min}}^{K_{max}} (E_0 - E_n) I_{0n}(K) \, dK,$$

† Loc. cit.

TABLE V

Oscillator Strengths, $f_{nl}(0)$, for the Shells of various Atoms.

	Be	B	C	N	O	F	Ne	Na	Mg
$1s$	1·000	0·931	0·861	0·792	0·723	0·653	0·584	0·584	0·584
$2s$	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000
$2p$		1·136	1·136	1·136	1·136	1·136	1·136	1·120	1·122
$3s$								1·040	1·040

	A	Cu	Kr	Ag	Xe	Au
$1s$	0·505	0·505	0·476	0·476	0·463	0·463
$2s$	0·565	0·565	0·462	0·462	0·420	0·420
$2p$	1·122	0·426	0·423	0·301	0·300	0·256
$3s$	1·040	1·040	0·566	0·566	0·446	0·446
$3p$	1·171	1·171	1·138	0·533	0·526	0·387
$3d$		1·418	1·407	1·407	1·405	0·408
$4s$			1·103	1·103	0·560	0·422
$4p$			1·220	1·220	1·070	0·450
$4d$				1·437	1·464	1·464
$4f$						1·712

which reduces to [cf. eq. (54)]

$$-\frac{dT}{dx} = \frac{16\pi^3 m\epsilon^4 N}{k^2 h^2} \sum \int_{K_{\min}}^{K_{\max}} f_{0n}(K)\,\frac{dK}{K}. \tag{60}$$

We cannot at once use the summation theorem (57) to evaluate the sum, as $K_{\min}$ is a function of n; we therefore divide the range of integration into two halves, according as K is greater or less than K_0, where

$$K_0 = \left\{\frac{8\pi^2 m}{h^2}|E_0|\right\}^{\frac{1}{2}}. \tag{61}$$

At first sight it would not appear to be necessary to take into account momentum changes greater than the quantity (61), since it was shown in previous sections that for such large values of K, $I_{0n}(K)$ is very small; but transitions in which there is a large momentum change are associated with large energy losses and so give appreciable contributions to the sum (60). In fact we shall show below that both ranges give approximately equal contributions to the energy loss. We denote the two contributions to the energy loss per cm. by E', E'' respectively.

For the calculation of E', the energy loss in transitions with small change of momentum, we expand e^{iKx} in powers of K as in equation (39). Then

$$E' = \frac{128\pi^5 m^2 N\epsilon^4}{k^2 h^4} \sum_n (E_n - E_0)|x_{0n}|^2 \int_{K_{\min}}^{K_0} \frac{dK}{K}. \tag{62}$$

We may now use the formula

$$\frac{8\pi^2 m}{h^2} \sum_n (E_n - E_0)|x_{0n}|^2 = 1,$$

which gives

$$E' = \frac{16\pi^3 m N \epsilon^4}{k^2 h^2}\left\{\log K_0 - \frac{8\pi^2 m}{h^2} \sum_n (E_n - E_0)|x_{0n}|^2\log K_{\min}\right\}. \quad (63)$$

Since we are dealing with fast electrons, we may use the approximate expression derived in § 1.1 for $K_{\min}$, viz.

$$K_{\min} = 4\pi^2 m(E_n - E_0)/kh^2.$$

Substituting in (63) and remembering that

$$-E_n = 2\pi^2 m\epsilon^4/h^2 n^2 = Rh/n^2, \qquad -E_0 = 2\pi^2 m\epsilon^4/h^2 = Rh,$$

we obtain finally

$$E' = \frac{16\pi^3 m N \epsilon^4}{k^2 h^2}\left\{\log K_0 - \frac{8\pi^2 m R}{h} \sum_n \left(1 - \frac{1}{n^2}\right)|x_{0n}|^2\log \frac{4\pi^2 m R}{kh}\left(1 - \frac{1}{n^2}\right)\right\}. \quad (64)$$

For the energy loss E'' due to large momentum changes we have

$$E'' = \sum_n \int_{K_0}^{K_{\max}} (E_n - E_0)I_{0n}(K)\,dK. \quad (65)$$

Making use of the summation formula (57), we obtain

$$E'' = \frac{16\pi^3 m\epsilon^4 N}{k^2 h^2} \int_{K_0}^{K_{\max}} \frac{dK}{K}.$$

In fixing $K_{\max}$ it is important to note that the expressions given by Born's approximation for $I_{0n}(K)$ are no longer valid if the momentum change is very great. We cannot, therefore, use the expression (13) for $K_{\max}$ in (65), but must employ the condition of conservation of momentum in the collision between the incident and atomic electron. Since the masses of the two electrons are equal, the maximum momentum which the atomic electron can receive will be half the total momentum. We take, then,

$$K_{\max} \simeq k.$$

Carrying out the integration, we obtain

$$E'' = \frac{16\pi^3 m^2 N \epsilon^4}{k^2 h^4}\{\log k - \log K_0\}. \quad (66)$$

Adding (66) and (64), we obtain for the total energy loss per cm. path

$$-\frac{dT}{dx} = \frac{16\pi^3 m^2 N \epsilon^4}{k^2 h^2}\left\{\log \frac{k^2 h^2}{4\pi^2 m R h} - \sum_n |x_{0n}|^2\left(1 - \frac{1}{n^2}\right)\log \frac{n^2-1}{n^2}\right\}. \quad (67)$$

The summation may be carried out numerically using the usual formulae for the matrix elements x_{0n}. The final result is

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2}\log\frac{mv^2}{cRh} \qquad (c = 1\cdot105). \qquad (68)$$

4.22. Complex Atoms. It is possible to generalize the formula (68) for complex atoms, if, as is usual, hydrogenic wave functions are assumed, and the excluded transitions allowed for. This has been done by Bethe, who finds

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2}\sum_{nl} f_{nl}(0)\left\{\log\frac{mv^2}{|E_{nl}|} + \frac{1}{f_{nl}(0)}\sum_{n'l'}\zeta_{nl}f_{nl,n'l'}(0)\log\frac{|E_{nl}|}{E_{n'l'} - E_{nl}}\right\}, \qquad (69)$$

where ζ_{nl}, f_{nl}, $f'_{nl,n'l'}$ are as previously defined in formulae (34), (53), and (58) respectively, and $f_{nl}(0)$ is the limit of the generalized oscillator strength for zero momentum change, i.e. is the usual oscillator strength. If we define the mean excitation energy A_{nl} of the nl shell by the formula

$$f_{nl}^{(0)}\log A_{nl} = f_{nl}^{(0)}\log|E_{nl}| + \sum_{n'l'}\zeta_{nl}f_{nl,n'l'}^{(0)}\log\frac{E_{n'l'} - E_{nl}}{|E_{nl}|}$$

we find for the stopping-power

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2}\sum_{nl} \frac{mv^2}{A_{nl}}.$$

TABLE VI

| | | | | $\left(\dfrac{dT}{dx}\right)\Big/(2\pi N Z\epsilon^4/mv^2)$. | |
| | | | | *Theoretical.* | |
v/c.	Gas.	u^2/v^2.	Observed.	Bohr.	Quantum Mechanics.
0·136	H_2	0·001	11·7	17·1	11·5
0·230	O_2	0·001 → 0·07	10·6	18·0	12·2
0·230	A	0·001 → 0·2	10·0	16·3	11·2

If we define a mean excitation energy E by the formula

$$Z\log E = \sum f_{nl}\log A_{nl},$$

we have

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2}Z\log\frac{mv^2}{E}. \qquad (70)$$

The difficulty in making quantitative use of this formula is to fix the value of E. The values of oscillator strengths given in Table V are only approximately correct for light elements and are very inaccurate

for heavy elements. Bloch† has attempted to remove this difficulty by using the Fermi-Thomas statistical model of the atom. He calculates the stopping-power by considering the disturbance of such a 'gas-sphere' atom by external forces and obtains the formula

$$-\frac{dT}{dx} = \frac{4\pi\epsilon^4 N}{mv^2} Z \log \frac{mv^2}{Z_\chi Rh}. \tag{71}$$

The constant χ may be determined from certain differential equations involving the Fermi-Thomas atomic field. These equations have not yet been solved, but Bloch shows that the dependence of E on Z, given by (71), is in agreement with experiment. The empirical value of χ which gives the best numerical agreement with observed values of $-dT/dx$ is also quite reasonable.

4.23. *Comparison with Experimental Values.* The application of the formulae (68) and (70) for the energy loss per cm. of fast electrons in (atomic) hydrogen and other gases has been considered exhaustively by Williams.‡ In order to compare the theoretical and experimental values it is necessary to increase the results by about 10 per cent. to allow for the fact that in practice the electron which emerges with the greater energy after the collision is taken as the β-particle. After applying this correction a very good agreement is obtained with experiment, as illustrated in Table VI. The values given by Bohr's classical theory§ are also included. As the validity of Born's first approximation, which is used throughout in the theory developed above, depends on the velocity of impact being great compared with the orbital velocity of the atomic electrons,‖ the ratio u^2/v^2 of the squares of these velocities is included in the table.

Further evidence in support of the quantum theory of the stopping-power of matter for fast charged particles will be discussed in Chapter XIII in connexion with the passage of heavy particles through matter.

4.24. *Relative Contribution of Light and Heavy Collisions to Stopping-power.* It was shown in § 3.31 that the number s_0 of primary ions produced per cm. path is given by

$$s_0 = \frac{2\pi N \epsilon^4}{mv^2} \sum_{nl}' \frac{c_{nl} Z_{nl}}{(-E_{nl})} \log \frac{2mv^2}{C_{nl}}, \tag{72}$$

† *Zeits. f. Physik,* **81** (1933), 363.
‡ *Proc. Roy. Soc.,* A, **135** (1932), 108.
§ *Phil. Mag.,* **25** (1913), 10; **30** (1915), 58. Bloch (*Ann. der Phys.,* **5** (1933), 285) has shown that Bohr's formula follows also in quantum mechanics when u^2/v^2 is small but $Z\epsilon^2/hv$ large.   ‖ Cf. Chap. IX, § 5.1.

where the quantities c_{nl}, C_{nl} are as defined in equations (49) and (50). The energy loss per primary ion produced is then given by $-\dfrac{dT}{dx}\Big/s_0$.

For nitrogen this gives, for electrons of 30,000 volts energy, an energy loss per primary ion produced, of roughly 80 volts, and for hydrogen 100 volts. This high value arises from the fact that a larger percentage of collisions lead to excitation than to ionization. The contribution to the energy loss per cm. due to heavy collisions (in which a fast† electron is emitted) is, moreover, quite considerable, owing to the great energy loss in the collision. It is given by

$$E'' = \frac{16\pi^3 m^2 N \epsilon^4}{k^2 h^4} \sum_{nl} Z_{nl} \int_{k_0}^{k} \frac{dK}{K}$$

$$= \frac{8\pi^3 m^2 N \epsilon^4}{k^2 h^4} \sum_{nl} Z_{nl} \log\left(\frac{k^2}{k_0^2}\right), \tag{73}$$

where $k_0^2 \simeq 8\pi^2 m |E_{nl}|/h^2$. Referring to the expression (68) for $-\dfrac{dT}{dx}$, we see that heavy collisions account for roughly half the total energy loss.

4.25. *Method of Impact Parameters.* For α-particles and fast electrons, the change of momentum of the incident particle in the great majority of inelastic collisions is small compared with its total momentum. In such problems it is in general permissible to treat the incident particle as a moving centre of force. It is permissible to do this if it is possible to form a wave packet small compared with the atom, and which will remain small while the wave packet passes the atom, and if further the main contributions to the excitation probability come from positions of the atomic electron which are outside the path of the wave packet.

The method of calculating the transition probability is given in Chap. XIV, § 2.2. In general it is not so convenient as the Born method, because the results have to be averaged over all values of the impact parameter. It may be shown directly that the two methods lead to the same result.‡

The method is interesting in that it shows the relative importance of close and distant collisions. Williams§ finds that for a 100,000-volt

† With energy great compared with the ionization potential.
‡ Mott, *Proc. Camb. Phil. Soc.*, **27** (1931), 553, and Frame, ibid., **27** (1931), 511.
§ *Proc. Roy. Soc.*, A, **139** (1933), 163.

electron traversing hydrogen, out of every fourteen atoms ionized or excited, only one lies on the direct path of the electron, and that four lie between $2 \cdot 5 \times 10^{-7}$ and 10^{-6} cm. Williams has also shown that for distant collisions the quantum theory gives the classical Bohr† formula, the discrepancy occurring for collisions in which the particle passes through the atom.

4.26. *Multiple Ionization and Excitation.* It is important to realize that multiple ionization has been neglected throughout this discussion. With the approximation of representing the wave functions of complex atoms by products of hydrogen-like wave functions the probability of multiple ionization vanishes, and before it is possible to estimate the magnitude of the effect more accurate wave functions must be used. It is unlikely that multiple excitation processes are important for light atoms owing to the weak coupling of the atomic electrons, but for heavy atoms their effect may be considerable.

5. Inelastic Collisions of Slow Electrons with Atoms

The theoretical investigation of inelastic collisions of slow electrons is much more complicated than for fast particles. Experimental evidence shows clearly that electron exchange becomes important, and the observations of Mohr and Nicoll‡ of the angular distribution of in-elastically scattered electrons in mercury vapour and in argon show that the distortion of the incoming and outgoing waves by the fields of the normal and excited atoms respectively must be taken into account (see below, § 5.3).

It was pointed out at the beginning of this chapter that according to Born's approximation the probability of excitation of a level belonging to a term system different from that of the initial state is zero. For impacts of sufficiently high velocity this is in agreement with observation, but for low-velocity collisions the excitation of these levels takes place quite readily, and at certain velocities may occur even more often than the excitation of a level of the same term series as the initial state. Thus in Fig. 33 we show the excitation probability velocity curves for the excitation of the 3^1P and 3^3P levels of helium from the ground 1^1S state, measured by Lees§ using optical methods (see Chap. IX, § 1). When the energy of the exciting electrons is greater than 100 volts, triplet excitation occurs very seldom compared with singlet excitation; but at voltages just above the excitation potential the reverse may be

† Loc. cit.   ‡ *Proc. Roy. Soc.*, A, **138** (1932), 229 and 469.
§ Ibid., **137** (1932), 173.

the case. This is a general feature of the observations of the excitation of various two-electron systems.† In all cases the triplet excitation curve rises to a maximum very rapidly at about a volt above the excitation potential, whereas the corresponding singlet curve attains a maximum much more gradually (except for S states). The magnitudes of the corresponding maxima are comparable in all cases.

If the coupling between spin and orbital motion is small, triplet excitation can only take place if electron exchange occurs on impact
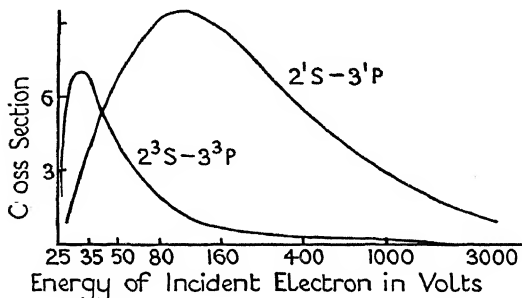
FIG. 33. Observed excitation functions of 3^1P and 3^3P levels in helium. The curves were obtained by measurement of the variation of the intensity of excitation of the spectral lines produced by optical transitions to the 2^1S, 2^3S levels respectively.

in such a way as to change the symmetry of the spin function of the atomic electrons. Therefore the experimental results show that the exchange process is important for low-velocity collisions. This process is not limited to excitation of levels of another term system, and must also be taken into account in singlet excitation.

Interesting results have been obtained by Mohr and Nicoll (loc. cit.), who investigated the angular distributions of electrons with initial energies between 50 and 120 volts scattered in various gases after exciting the most probable level. Some of the observed curves are illustrated in Fig. 34. For the heavier gases the maxima and minima are very noticeable. The similarity of the diffraction effects observed in angular distributions of elastically and inelastically scattered electrons of the same incident velocity indicates that the two effects are due to the same cause, the distortion of the electron waves by the atomic field. This will be discussed further in § 5.3.

† Hughes and Lowe, *Proc. Roy. Soc.*, A, **104** (1923), 480; Skinner and Lees, *Nature*, **123** (1929), 836, and Lees, *Proc. Roy. Soc.*, A, **137** (1932), 173; Hanle, *Zeits. f. Physik*, **56** (1929), 94; Michels, *Phys. Rev.*, **36** (1930), 1362; Thieme, *Zeits. f. Physik*, **78** (1932), 412.
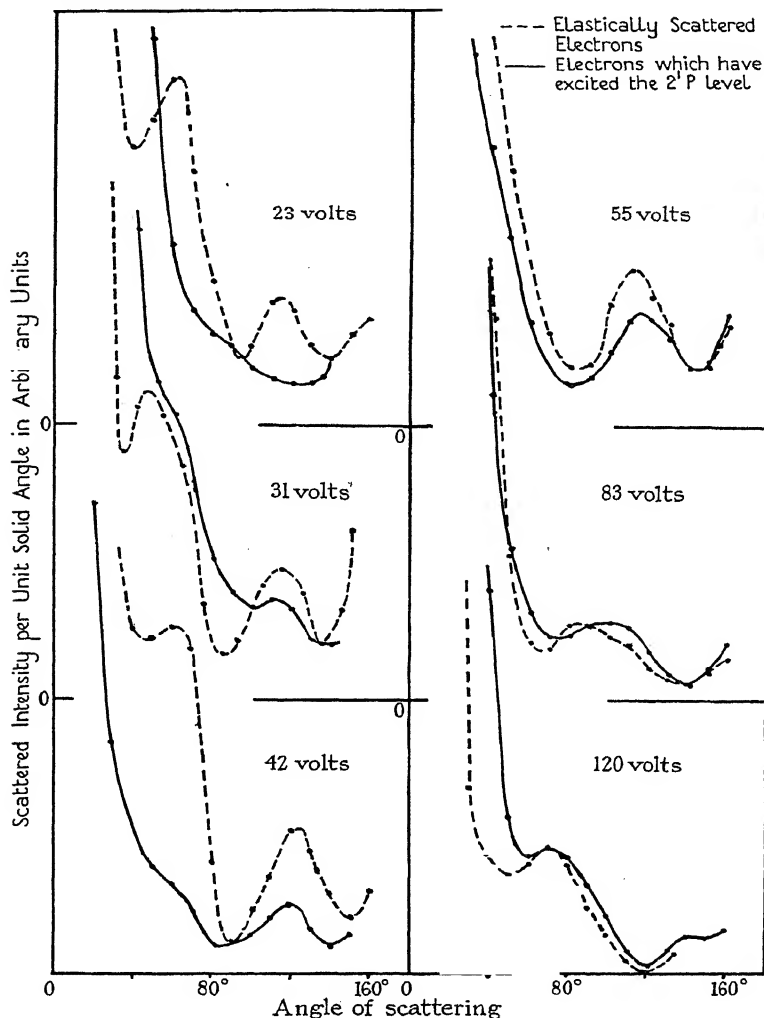
FIG. 34. Observed angular distributions of electrons scattered by mercury vapour.

5.1. *Application of Theory of Collisions.*

A completely satisfactory method of dealing with slow inelastic electron collisions does not yet exist, but by using the general theory of Chapter VIII we may obtain approximate formulae for the probabilities

involved. The scattering of electrons which have excited the nth state of atoms of hydrogen and helium may be described by means of two wave functions $F_n(\mathbf{r_1})$, $G_n(\mathbf{r_2})$ which have the asymptotic forms

$$F_n(\mathbf{r_1}) \sim f_n(\theta_1, \phi_1) r_1^{-1} \exp(ik_n r_1),$$

$$G_n(\mathbf{r_2}) \sim g_n(\theta_2, \phi_2) r_2^{-1} \exp(ik_n r_2). \tag{74}$$

The differential cross-section for excitation of the nth state is then given by

$$I_n(\theta) = \frac{1}{4}\frac{k_n}{k}\{3|f_n(\theta, \phi) + g_n(\theta, \phi)|^2 + |f_n(\theta, \phi) - g_n(\theta, \phi)|^2\}, \qquad \text{for hydrogen,}$$

$$= \frac{k_n}{k}|f_n(\theta, \phi) - g_n(\theta, \phi)|^2, \qquad \text{for helium.} \tag{75}$$

In Chapter VIII, equations (61) and (62), these functions are shown to satisfy the equations

$$[\nabla_1^2 + k_n^2]F_n(\mathbf{r_1}) = -\frac{8\pi^2 m\epsilon^2}{h^2} \int \left(\frac{1}{r_1} - \frac{1}{r_{12}}\right)\Psi(\mathbf{r_1}, \mathbf{r_2})\psi_n^*(\mathbf{r_2})\, d\tau_2,$$

$$[\nabla_2^2 + k_n^2]G_n(\mathbf{r_2}) = -\frac{8\pi^2 m\epsilon^2}{h^2} \int \left(\frac{1}{r_2} - \frac{1}{r_{12}}\right)\Psi(\mathbf{r_1}, \mathbf{r_2})\psi_n^*(\mathbf{r_1})\, d\tau_1. \tag{76}$$

The function Ψ is the solution of the wave equation for the complete system of atom and incident electron. To solve these equations we must, as in Chap. X, § 8, substitute some approximate form for Ψ on the right-hand side of (76). We shall set on the right-hand side,

$$\Psi = F_0(\mathbf{r_1})\psi_0(\mathbf{r_2}) + F_n(\mathbf{r_1})\psi_n(\mathbf{r_2}) + G_n(\mathbf{r_2})\psi_n(\mathbf{r_1}). \tag{77}$$

Here $F_0(r)$ is the solution representing an incident wave and a scattered wave, as discussed in Chapter II, of

$$\left(\nabla^2 + k^2 - \frac{8\pi^2 m}{h^2}V_{00}\right)F_0 = 0. \tag{78}$$

We note that (77) is not the same approximation as that used in Chap. X, § 8, in dealing with the elastic collisions. By including terms in ψ_n, we ensure that on the right-hand side of (76) all diagonal elements V_{ss} of the interaction energy shall be included. The only non-diagonal matrix elements are those, V_{0n}, which refer to the initial state of the atom.

On substitution in (76) we obtain, by following a similar procedure

to that used in the consideration of the elastic exchange, the equation

$$\left[\nabla_1^2+k_n^2-\frac{8\pi^2 m}{h^2}V_{nn}(r_1)\right]\{F_n(\mathbf{r}_1)\pm G_n(\mathbf{r}_1)\}$$

$$=-\frac{8\pi^2 m\epsilon^2}{h^2}\Big\{\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\pm F_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)+$$

$$+\{G_n(\mathbf{r}_2)\pm F_n(\mathbf{r}_2)\}\psi_n(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)]\,d\tau_2\Big\}, \tag{79}$$

The third term on the right-hand side makes further approximation difficult except for high velocities of impact. In this case we may neglect the effect of the atomic field in the zero-order approximation, and write on the right-hand side of (79)

$$F_0(\mathbf{r}_1)=\exp(ik\mathbf{n}_0\cdot\mathbf{r}_1), \qquad G_n(\mathbf{r}_2)=0.$$

We then obtain

$$(\nabla^2+k_n^2)\{F_n(\mathbf{r}_1)\pm G_n(\mathbf{r}_1)\}=-\frac{8\pi^2 m\epsilon^2}{h^2}\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)\times$$

$$\times\{\exp(ik\mathbf{n}_0\cdot\mathbf{r}_1)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\pm\exp(ik\mathbf{n}_0\cdot\mathbf{r}_2)\psi_0(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)\}\,d\tau_2. \tag{80}$$

Solving this equation by the method of Chap. VI, § 4, we have

$$f_n(\theta,\phi)\pm g_n(\theta,\phi)$$

$$=\frac{2\pi m\epsilon^2}{h^2}\int\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)[\exp\{i(k\mathbf{n}_0-k_n\mathbf{n}_1)\cdot\mathbf{r}_1\}\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\pm$$

$$\pm\exp\{i(k\mathbf{n}_0\cdot\mathbf{r}_2-k_n\mathbf{n}_1\cdot\mathbf{r}_1)\}\psi_0(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2)]\,d\tau_1\,d\tau_2. \tag{81}$$

For low-velocity impacts with two-electron atoms we are concerned with the differences of F_n and G_n only, and if they interfere to give only a small collision probability, we may neglect the third term and obtain, in the same way as for the case of elastic exchange,

$$f_n(\theta,\phi)-g_n(\theta,\phi)$$

$$=\frac{2\pi m\epsilon^2}{h^2}\int\int\left(\frac{1}{r_1}-\frac{1}{r_{12}}\right)[F_0(r_1,\theta_1)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\mathfrak{F}_n(r_1,\pi-\Theta_1)-$$

$$-\mathfrak{F}_n(r_1,\pi-\Theta_1)F_0(r_2,\theta_2)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_1)]\,d\tau_1\,d\tau_2, \tag{82}$$

where $\mathfrak{F}_n(r,\theta)$ is the solution of the homogeneous equation

$$\left[\nabla^2+k_n^2-\frac{8\pi^2 m}{h^2}V_{nn}(r)\right]\mathfrak{F}_n(r,\theta)=0,$$

which has the asymptotic form

$$\mathfrak{F}_n(r,\theta)\sim\exp ik_n z+r^{-1}\exp ik_n r\times\text{function of }\theta,\phi,$$

and $$\cos\Theta_1=\cos\theta\cos\theta_1+\sin\theta\sin\theta_1\cos(\phi-\phi_1).$$

The interpretation of the formulae (81) and (82) is interesting. The

first term represents the directly scattered waves, the second the electron exchange. They are both of the form expected, being the integrals of the interaction energy over the initial and final wave functions of the system. The formula (82) differs from (81) in that the former includes the effect of the potential field V_{nn} on the outgoing wave and of the field V_{00} on the incident wave.

Before discussing the application of these formulae we shall consider briefly the approximations involved. Firstly we notice that the expression (77) assumed for Ψ does not satisfy the orthogonality relations

$$\int \{\Psi - F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)\}\psi_n^*(\mathbf{r}_2) \, d\tau_2 = 0,$$

$$\int \{\Psi - G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1)\}\psi_n^*(\mathbf{r}_1) \, d\tau_1 = 0. \tag{83}$$

As a consequence, contributions to the integrals in (81) and (82) arise from terms in the interaction energy which would not be effective if the relations (83) were satisfied. For reasonably high velocities of impact the errors made will be small, but for electrons with energies near the energy of excitation the errors made may be large. This difficulty was discussed in Chapter X in connexion with elastic exchange, and it is not easy to overcome.

Secondly, it is difficult to justify the use of (82) throughout the range of values of F_n and G_n owing to the uncertain magnitude of the third term which is neglected. By converting (79) into an integral equation we see that this term represents the probability of an exchange of electrons taking place *after* the initial inelastic scattering which leads to the wave $F_n(\mathbf{r}_2) \pm G_n(\mathbf{r}_2)$. Its effect may be small, but this is by no means certain.

Finally, we notice that we assume that all non-diagonal matrix elements are small and so neglect the effect of the reaction of the waves F_n, G_n on the incident and elastically scattered wave F_0. This corresponds to weak coupling between the two sets of waves, but actually in certain cases it may be necessary to assume 'close coupling' corresponding to a large value of the non-diagonal matrix element V_{0n}. It will be shown below that the experimental evidence does indicate the necessity for including such effects.

The approximation of neglecting all non-diagonal matrix elements except V_{0n} also fails to include the reaction of the other inelastically scattered waves on the $0 \to n$ excitation. These last approximations differ from those made above, as they are not introduced by exchange considerations but are inherent in the method of distorted waves (Chap. VIII, § 3.1) and have already been discussed in that connexion.

5.2. *Calculations for Helium and Comparison with Experiment.*

The singlet and triplet excitation cross-sections for helium were first calculated as functions of the velocity of the exciting electron by Massey and Mohr† using the approximate formula (81), and these calculations have been extended to cover a wide range of velocities and a large number of excited states.
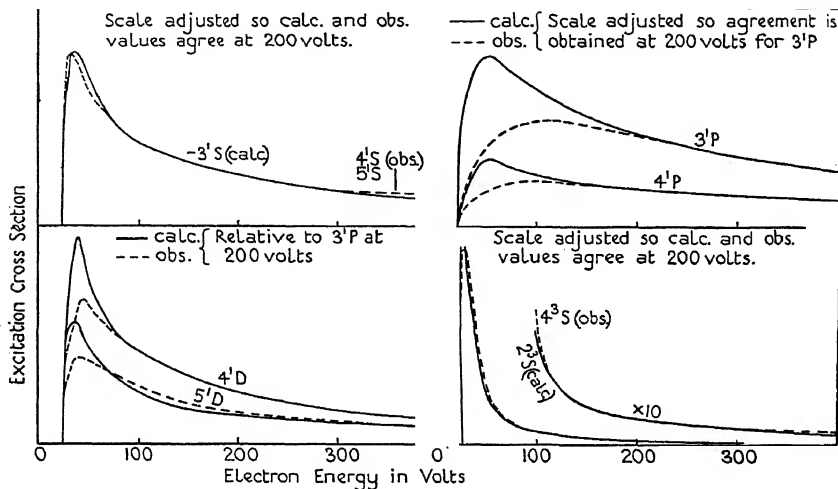
FIG. 35. Comparison of observed and calculated excitation cross-section velocity curves.

A number of general features of the experimental results are reproduced. From formula (81) it may be shown that the triplet excitation probability falls off as v^{-4}, v^{-6}, v^{-8} for S, P, D states respectively, in sharp contrast to the variation as v^{-2}, $v^{-2}\log \alpha v$, v^{-2} for the corresponding singlet state, v being the incident electron's velocity.

In the case of both ^1S and ^3S states detailed agreement is obtained between theory and experiment down to quite low velocities of impact, but for ^1P and ^1D states the agreement becomes unsatisfactory for electrons of energy less than 100 and 75 volts respectively. This is illustrated in Fig. 35. Referring to this figure we see that as the electron energy is reduced below 100 volts the calculated probabilities of excitation of the P-levels become considerably greater than the observed. This effect is only apparent for ^1D levels at lower velocities and for S states it is doubtful if there is any great discrepancy at any velocity.

† *Proc. Roy. Soc.*, A, **132** (1931), 605; ibid., **140** (1933), 613.

We showed in § 3.2 and § 3.3 of this chapter that the same behaviour is a feature of the ionization and X-ray excitation probabilities, and it seems that Born's formula is least valid for the calculation of transition probabilities involving optically allowed transitions. Examining the approximations we have introduced, we see that this almost certainly implies that the failure of the theory in such cases is due to the assumption that V_{0n} is small. Actually, for the excitation of optically allowed levels V_{0n} vanishes only as r^{-2} for large r, and such a field has a large scattering power (thus the elastic cross-section for such a field is infinite, cf. Chap. II, § 3). To improve the theory it would be necessary to solve simultaneous equations of the same form as those discussed in Chap. VIII, § 3.2. It was shown there (cf. Chap. VIII, Fig. 11, also Chap. XIII, § 3.31) that accurate solution of these equations will lead to a smaller probability of excitation than that given by Born's approximation, just as is required from the above experimental results. For D levels V_{0n} vanishes as r^{-4} for large r, and this field will have a much smaller scattering power than that corresponding to P excitation. We should thus expect Born's approximation to agree with experiment down to much lower velocities for D excitation, while for S excitation, for which V_{0n} vanishes as $e^{-\lambda r}$ for large r, we expect very little deviation from the simple theory. This, again, is in agreement with the observed results.

The calculated relative magnitudes of triplet and singlet excitation probabilities for electrons of energy greater than 100 volts are in rough agreement with experiment, but it appears that the observed excitation curves for ^3P levels fall off much more slowly with velocity than the calculated curves. The reason for this discrepancy is not clear but is probably due to secondary processes occurring in the experimental apparatus.

The excitation of the 2^1P and 2^3P levels has also been considered by the same authors[†] using formula (82). The wave function $\mathfrak{F}_n$ was calculated numerically by Macdougall[‡] and the integration of (82) carried out by numerical methods. The chief interest of this calculation is that it includes the distortion of the incident and outgoing waves by the atom and should include the diffraction effects to be expected. For 50-volt electrons an angular distribution is predicted which is of the form observed by Mohr and Nicoll (loc. cit.), becoming approximately uniform for large angles of scattering but with a faint maximum at 90°.

† Proc. Roy. Soc., A, 139 (1932), 187.
‡ Proc. Camb. Phil. Soc., 28 (1932), 341.

5.3. *Excitation of Heavy Atoms.*

Calculations for the excitation of the $2P$ levels of mercury have been carried out by Penney,† who also used the formula (81). The chief interest of his calculations is his use of atomic wave functions which include terms arising from the interaction of spin and orbital motion. These are quite appreciable for such a heavy atom as mercury. As a consequence the wave functions for the triplet state 2^3P_1 are not completely antisymmetrical in the orbital wave functions, and so this state can be excited without electron exchange. The excitation of this triplet level therefore persists at high velocities. The calculated ratio of the intensities of the various levels agrees well with experiment even at exciting energies as low as 10 volts. The form of the excitation-velocity curves for all the levels also agrees qualitatively with the observations.

We now consider the diffraction effects observed by Mohr and Nicoll ‡ in electrons scattered inelastically by atoms. If we neglect exchange effects (which is legitimate at moderate to high velocities of impact), the intensity of scattering of electrons which have excited the nth state of a given atom is given per unit solid angle by

$$I_n(\theta) = \frac{k_n}{k} \frac{4\pi^2 m^2}{h^4} \left| \int V_{0n}(\mathbf{r}')F_0(r',\theta')\mathfrak{F}_n(r',\pi-\Theta)\,d\tau' \right|^2, \qquad (84)$$

where
$$V_{0n}(\mathbf{r}) = \int V(\mathbf{r},\mathbf{r}_a)\psi_0(\mathbf{r}_a)\psi_n^*(\mathbf{r}_a)\,d\tau_a.$$

the suffix a distinguishing the coordinates of the atomic electrons. The functions $F_0(r,\theta)$, $\mathfrak{F}_n(r,\Theta)$ can be written in the form

$$F_0(r,\theta) = e^{ikr\cos\theta} + \sum_s \left[F_0^s - \sqrt{\left(\frac{2\pi}{kr}\right)}J_{s+\frac{1}{2}}(kr) \right](2s+1)i^s P_s(\cos\theta), \quad (85)$$

$$\mathfrak{F}_n(r,\pi-\Theta) = e^{-ik_n r\cos\Theta} + \sum_s \left[\mathfrak{F}_n^s - \sqrt{\left(\frac{2\pi}{k_n r}\right)}J_{s+\frac{1}{2}}(k_n r) \right](2s+1)i^{-s}P_s(\cos\Theta), \qquad (86)$$

where the first term denotes a plane wave undisturbed by the atomic field and the series represents the disturbance of the plane waves by the fields of the normal and excited atoms. Substituting in (84), we find that

$$I_n(\theta) = \frac{k_n}{k} \frac{4\pi^2 m^2}{h^4} \left| \int V_{0n} \exp\{i(kr'\cos\theta' - k_n r'\cos\Theta)\}\,d\tau' + \right.$$

$$\left. + \sum_s P_s(\cos\theta)\int V_{0n}H_s(r',\theta',\phi')\,d\tau' \right| \qquad (87)$$

† *Phys. Rev.*, 39 (1932), 467.

where H_s is a certain function of r', θ', ϕ'. The first term in the integral is just that given by Born's formula and its behaviour has been discussed in § 2 of this chapter. At angles of scattering greater than 30° it is negligibly small and so the main contribution comes from the series. The number of harmonics which are important in this series determines the diffraction effects at angles greater than 30°. Now, if the energy of the incident electron is great compared with the excitation energy, $k_n \simeq k$, and also the fields of the normal and excited atoms will be effectively the same. In this case the same number of terms in the series (85) and (86) will be required, and these will be of the same relative importance as for the elastic scattering, which is described by $F_0(r, \theta)$. The diffraction effects at large angles will therefore be very similar to those occurring in the elastic scattering. This is the observed result.

For low velocities this similarity will disappear, as the field V_{nn} has a much greater spread than V_{00}, and so will affect more harmonics of $\mathfrak{F}_n$ than V_{00} will of F_0. The difference between k_n and k will also be important at these velocities. This result is a feature of the observations in mercury vapour. (Cf. Fig. 34, in which it will be seen that the angular distributions for the inelastically scattered electrons resemble those for the elastically scattered at voltages above 55 volts but become more and more dissimilar as the voltage decreases below this.)

5.4. *Summary.*

We have shown above that, for slow electronic collisions with atoms, Born's approximation fails in two ways. It predicts too great a value for the inelastic cross-section, and fails to account for the maxima and minima in the inelastic angular distributions. We have shown above how more accurate solutions of the differential equations can account, at least qualitatively, for these effects.

A suggestive model by means of which a mental picture of the processes involved can be formed has been given by Massey and Mohr.† In the Born approximation, and also in the method of distorted waves, the transition probabilities $I_n(\theta)$ are of the form of the square of the modulus of a matrix element involving the initial and final states of the scattered electron. Massey and Mohr show that the correction terms in the higher approximations may be interpreted as giving the probability that an electron, which has lost energy to an atom, may regain that energy before it leaves the atom in question. Such an effect

† *Proc. Roy. Soc.*, A, **140** (1933), 613.

will obviously tend to reduce the inelastic cross-section. The authors cited also explain the fact that more electrons than Born's method predicts† are elastically scattered at small angles, by assuming that some fraction of the inelastically scattered electrons, of which most are scattered through small angles, regain their lost energy before leaving the atom.

† Cf. Chap. IX, § 5.

XII

THE COLLISION OF ELECTRONS WITH MOLECULES

1. The phenomena considered in this chapter may be classified as follows:

1. Diffraction effects due to the presence of two or more nuclei. Such effects are analogous to the optical case of diffraction by a number of slits.

2. Dissociation on impact. The application of quantum mechanics to molecules has shown that there exist, for given nuclear separation, a number of electronic states which do not give rise to a stable molecule, as well as those which do. A transition from a stable state to an unstable one results in dissociation of the molecule. The stable and unstable states belong in many cases to two non-combining term systems; nevertheless the occurrence of electron exchange on impact introduces the possibility of dissociation of the molecule in this manner. Dissociation by impact without exchange may also occur accompanying ordinary excitation or ionization.

3. Excitation of internal molecular motion. For incident electrons with energies comparable with the energy of the nuclear vibration or rotation, there is a possibility of energy interchange with these motions.

We shall now discuss these phenomena from a theoretical point of view. It is at once clear that the theory of scattering of electrons by molecules will be much more complicated than for the scattering by atoms. The molecular field is not spherically symmetrical, and the internal motions of the molecule cannot be neglected for low-voltage impacts.

For our purpose we require an expression for the molecular field; the method of the self-consistent field has not yet been applied. For the hydrogen molecule approximate wave functions have been obtained by Wang† and by N. Rosen,‡ using variation methods; thus the field of this molecule is known to a fair degree of approximation. This method becomes too complicated for any other molecule; but Hund§ has recently applied the statistical method of Thomas and Fermi to the problem. He finds that the molecular field of a symmetrical diatomic molecule can be represented with quite high accuracy by the sum of two fields which have spherical symmetry about the respective nuclei, and gives numerical data for the nitrogen and fluorine molecules.

† *Phys. Rev.*, **31** (1928), 579.   ‡ Ibid. **38** (1931), 2099.
§ *Zeits. f. Physik*, **77** (1932), 12.

With the approximate fields discussed above, scattering formulae may be obtained without difficulty by Born's approximate method. When we attempt to obtain a more accurate scattering formula, by an extension of the method of Faxén and Holtsmark (Chapter II), we encounter the difficulty that the wave equation for the motion of an electron in the field of a molecule is not separable as in the case of atomic fields; to obtain a solution one must use a very much simplified form for the field, as will be shown in § 5.

We shall first consider the application of Born's approximation.

2. Scattering by an Axially Symmetrical Field†

It was shown in Chap. VII, § 1, that, if Born's formula is applicable, the scattering by a spherically symmetrical field is a function of $v \sin \frac{1}{2}\theta$ only, where v is the velocity of the incident electron and θ the angle of scattering. It may be shown that the scattering by a number of similar independent axially symmetrical fields will also be a function of $v \sin \frac{1}{2}\theta$ only, provided that the directions of the axes of the fields are distributed at random (as in the case of gas molecules).

If the potential of such a field is given by

$$V(r, \theta, \phi) = \sum_n V_n(r) P_n(\cos u),$$

where u is measured with respect to the axis of symmetry, the differential cross-section for scattering by such a field, averaged over all directions of the axis, is given by

$$I(\theta)\, d\omega = \frac{4\pi^2 m^2}{h^4} \sum_0^\infty \{F_n(v \sin \tfrac{1}{2}\theta)\}^2\, d\omega,$$

where

$$F_n(v \sin \tfrac{1}{2}\theta) = \frac{2\pi}{2n+1} \left(\frac{\pi}{k \sin \frac{1}{2}\theta}\right)^{\frac{1}{2}} \int_0^\infty V_n(r) J_{n+\frac{1}{2}}(2kr \sin \tfrac{1}{2}\theta) r^{\frac{3}{2}}\, dr.$$

k is, as usual, written for $2\pi m v / h$.

It is possible to obtain a relation between the X-ray and electron scattering, similar to that obtained in the case of atoms.‡ Thus for homonuclear diatomic molecules we have the relation§ (not averaged over all orientations)

$$I(\theta)\, d\omega = \frac{}{2m^2 v^4 \sin^4 \frac{1}{2}\theta} \left| 2Z \cos\left\{\frac{\pi}{\lambda}(\mathbf{n_0} - \mathbf{n_1}) \cdot \mathbf{d}\right\} - F \right|\, d\omega,$$

where $\mathbf{d}$ is the vector nuclear separation, Z the nuclear charge, F the

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† Massey and Mohr, *Proc. Roy. Soc.*, A, **136** (1932), 258.
‡ See Chap. VII, § 1.   § Massey and Mohr, loc. cit.

X-ray structure factor of the molecule, and λ the wave-length of the scattered waves. $\mathbf{n}_0$ and $\mathbf{n}_1$ are unit vectors in the direction of incidence and of scattering respectively.

3. Elastic Scattering by Molecular Hydrogen

It has been pointed out in § 1 that only for the simplest molecule H_2 has it proved possible to obtain even an approximate analytical formula for the potential $V(r, \theta)$.

If $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is the wave function of the ground state of the molecule, we have in this case

$$V(r, \theta) = \epsilon^2 \int\int \left(\frac{1}{r} + \frac{1}{p} - \frac{1}{|\mathbf{r}-\mathbf{r}_1|} - \frac{1}{|\mathbf{r}-\mathbf{r}_2|}\right)\psi_0(\mathbf{r}_1, \mathbf{r}_2)\psi_0^*(\mathbf{r}_1, \mathbf{r}_2)\, d\tau_1\, d\tau_2, \quad (1)$$

where we denote distances from the nuclei by r, p respectively, and the molecular electrons by suffixes 1, 2. For $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$ we may use a function obtained by Wang† by a variation method. Wang gives

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = Z^3\left[\frac{1}{2\pi}\{1 + e^{-2Zd}(1 + Zd + \tfrac{1}{3}Z^2d^2)^2\}\right]^{\frac{1}{2}}[e^{-Z(r_1+p_2)} + e^{-Z(r_2+p_1)}], \quad (2)$$

with $Z = 1 \cdot 166/a_0$. d is the equilibrium nuclear separation and is approximately equal to $\tfrac{3}{2}a_0$.

If we substitute the expression (2) for $\psi_0(\mathbf{r}_1, \mathbf{r}_2)$ in (1), it is possible to calculate the differential elastic cross-section $I(\theta)\, d\omega$ for hydrogen molecules of random orientation, providing that the Born formula is valid. This was first done by Massey‡ for a certain range of velocities and angles of scattering, and then extended by Massey and Mohr§ to cover the whole range of values of $v \sin \tfrac{1}{2}\theta$. The final formula for the differential cross-section averaged over all orientations of the nuclear axis is given by

$$(1 + \sin x/x)[I_1 + I_2] + \text{terms of higher order,}$$

where

$$I_1 = \pi^2 Z^{-3}(2Z^2 + k^2\sin^2\tfrac{1}{2}\theta)(Z^2 + k^2\sin^2\tfrac{1}{2}\theta)^{-2},$$

$$I_2 = \frac{\pi^2 S}{Z^3 k^2\sin^2\tfrac{1}{2}\theta} - \left(\frac{4\pi}{k\sin\tfrac{1}{2}\theta}\right)^{\frac{5}{2}} \int_0^\infty e^{-Zr}f_0(r, d)J_{\frac{1}{2}}(2kr\sin\tfrac{1}{2}\theta)r^{\frac{3}{2}}\, dr. \tag{3}$$

In these formulae,

$$S = e^{-Zd}(1 + Zd + \tfrac{1}{3}Z^2d^2)$$

$$f_0(r, d) = e^{-Zd}(Z^2rd)^{-1}\{(1 + Zd)\sinh Zr - Zr\cosh Zr\} \qquad (r < d),$$

$$= e^{-Zr}(Z^2rd)^{-1}\{(1 + Zr)\sinh Zd - Zd\cosh Zd\} \qquad (r > d).$$

† *Phys. Rev.*, **31** (1928), 579.   ‡ *Proc. Roy. Soc.*, A, **129** (1930), 616.
§ *Ibid.* **135** (1932), 258.

The significance of the various terms is of interest. I_1 gives the scattering by the two atoms considered separately, but with effective nuclear charge 1·166; I_2 gives the effect of the molecular binding in producing a concentration of charge between the nuclei, and $1+\sin x/x$ is the diffraction factor due to the two scattering centres.

In order to illustrate the relative importance of these terms, the scattering by the molecule is compared in Fig. 36 with the scattering by two separated hydrogen atoms for various values of $v\sin\frac{1}{2}\theta$. Without
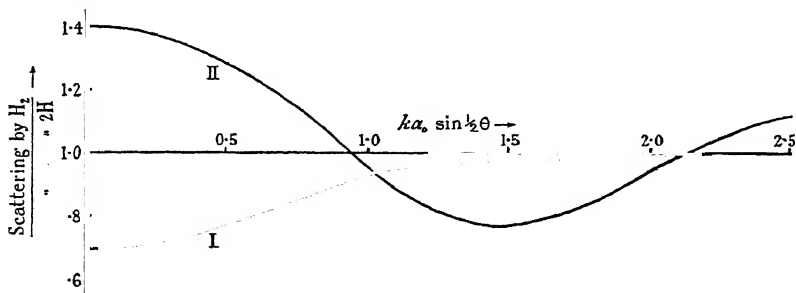
FIG. 36. Illustrating the ratio of scattering by H_2 to the scattering by 2H. I. Without the diffraction factor $1+\sin x/x$. II. With the diffraction factor $1+\sin x/x$.

the diffraction factor, it is seen that the scattering by the molecule falls below that by the separated atoms for small values of $v\sin\frac{1}{2}\theta$. This is due to the molecular binding, which produces an increased concentration of charge between the two atoms, and so reduces the effective collision area. On introducing the diffraction factor the ratio oscillates about the mean value unity. Apart from the diffraction factor, the scattering is represented very well by that from two atoms of effective nuclear charge 1·166.

We may now compare the formula (3) with the results of experiment. It was shown in Chap. IX, § 3.2, that the observed low-voltage angular distributions for molecular hydrogen are not in agreement with the Born formula, and, assuming that the molecular binding has only a small effect, the discrepancy was explained in terms of higher approximations in the theory in Chap. X, § 9. For higher voltages the measurements of Arnot† with 80-, 200- and 400-volt electrons show good agreement with the formula (3). This is illustrated in Fig. 37, in which curves calculated for atomic hydrogen are also given. It is difficult to choose between the theoretical curves for the atom and the molecule; if anything, the experiments seem to favour the latter.

† *Proc. Roy. Soc.*, A, **133** (1931), 615.
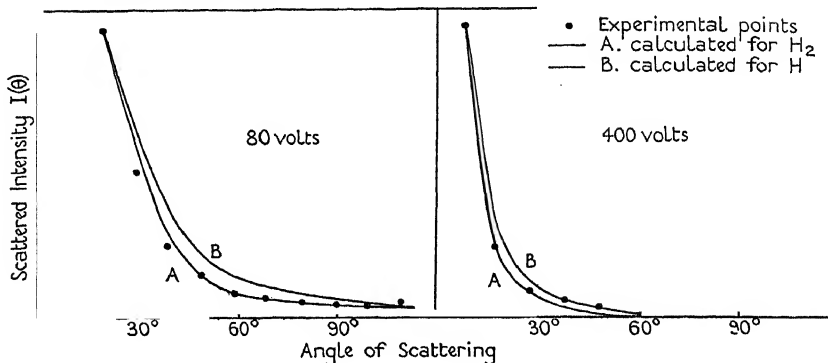
FIG. 37. Angular distributions of electrons scattered elastically by hydrogen.

The scales of the curves are adjusted so that both pass through the experimental points at the minimum scattering angle.

4. Scattering by Complex Molecules

It is clear that one cannot expect to find evidence of the two-centre diffraction effects by experiments in molecular hydrogen, owing to the very rapid decrease of scattered intensity with angle, but for heavier molecules the effects may readily be observed.

An obvious feature of the calculations for molecular hydrogen was the small effect of the molecular binding. For fast electrons the effect is completely negligible except at very small angles. In order to investigate the generality of this result the calculations may be extended to the scattering by nitrogen. Hund (loc. cit.) has shown that the potential of the molecular field is given approximately by

$$V(r, \theta, \phi) = 2\epsilon Z d^{-1}\{v(r) + v(p)\},\tag{4}$$

where Z is the nuclear charge, d the nuclear separation, and r, p the distances from the two nuclei. As the functions $v(r)$, $v(p)$ are spherically symmetrical with respect to the respective nuclei, the scattered intensity, averaged over all orientations of the nuclear axis, is given by

$$I(\theta) = \frac{32\pi^4 m^2 \epsilon^4 Z^2}{k^2 d^2 h^4 \sin^2 \frac{1}{2}\theta}\left(1 + \frac{\sin x}{x}\right)\left\{\int v(r)\sin(2kr \sin \tfrac{1}{2}\theta)\,dr\right\}^2.\tag{5}$$

Using the table of values of $v(r)$ given by Hund, we may calculate $I(\theta)$ by numerical methods. The results of the calculation† show that the effect of the binding is again quite small and may be neglected in a first approximation.

It is probable that this result will apply to all molecules. For homo-

† Bullard and Massey, *Proc. Camb. Phil. Soc.*, in course of publication.

nuclear diatomic molecules we may, then, write the differential cross-section for the scattering of fast electrons in the form

$$I(\theta) = 2I_a(\theta)[1+\sin x/x], \qquad (6)$$

I_a being the cross-section for the separate atom, and x being written for $4\pi d \sin\frac{1}{2}\theta/\lambda$.

This formula may be generalized for polyatomic molecules by means of a formula, due to Debye,† for the scattering of X-rays by a system
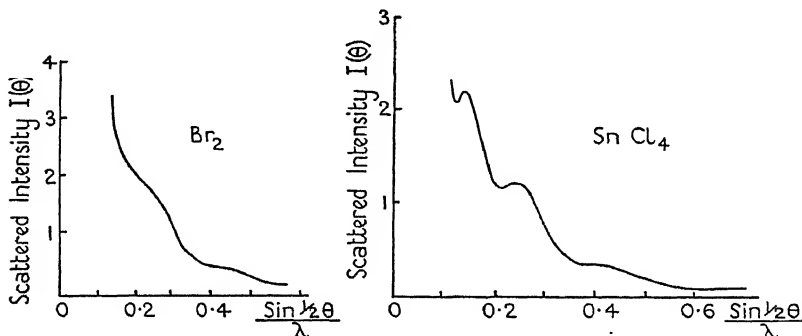
FIG. 38.   Illustrating diffraction of electrons by heavy molecules.
(Note that λ is measured in units of a_0.)

of scattering centres. For a molecule with n atoms the scattered intensity is given by

$$I(\theta) = \sum_{i=1}^{n} \sum_{j=1}^{n} J_i J_j^* \qquad (7)$$

where $x_{ij} = 4\pi l_{ij} \sin\frac{1}{2}\theta/\lambda$. In this formula l_{ij} is the distance between the nuclei i, j; and J_i is the amplitude of the wave which would be scattered by the atom i alone, i.e. such that $|J_i|^2 \, d\omega$ is the differential cross-section corresponding to the ith atom.

The amplitudes J_i are readily obtainable by the use of the Hartree or Fermi-Thomas atomic fields and Born's formula, as described in Chap. IX, § 4. As an illustration of the type of angular distribution obtained, the calculated form of $I(\theta)$ for Br_2 and for $SnCl_4$ is illustrated in Fig. 38 as a function of $\sin\frac{1}{2}\theta/\lambda$. The appearance of maxima and minima is particularly well marked in the case of the heavier molecule. The position of the maxima and minima will depend on the molecular structure; this enables the structure of a given molecule to be determined from experimental investigations of the scattering of electrons

† *Ann. der Physik,* **46** (1915), 809.

by it. This has been done by Wierl† for a large number of molecules, and it has been proved possible to answer many questions of importance in organic chemistry in this way. Thus it has been established that the benzene molecule has a plane configuration, and the tetrahedral model of the carbon valencies has been confirmed. Complicated structures may be investigated and it is possible to determine the type of binding between the different atoms by measuring the separations. It is found, for example, that there is a characteristic separation of two carbon atoms joined by a single bond, a second characterizing a double bond, and so on. For further details the reader is referred to the original papers.

5. Application of Faxén and Holtsmark's Method

As pointed out in § 1, the generalization of Faxén and Holtsmark's method to apply to the scattering of electrons by a molecular field is not possible without great simplification of the field. The question of calculating the scattering of slow electrons by a sufficiently representative molecular field has been considered in great detail by Stier.‡

Using spheroidal coordinates ρ, μ, ϕ defined by

$$\rho = (r+p)/d, \qquad \mu = (r-p)/d, \tag{8}$$

it can be shown that the wave equation for the elastic scattering is separable if the potential has the form

$$V(\rho, \mu) = -2Z\epsilon^2 d^{-1} \rho f(\rho)/(\rho^2 - \mu^2). \tag{9}$$

Proceeding by analogy with the method used by Allis and Morse§ for the scattering by atoms, Stier takes for the molecular field the form (9) when $\rho \leqslant \rho_0$, and V equal to zero for $\rho > \rho_0$; ρ_0 is a constant. For f Stier takes

$$f(\rho) = (\rho_0 - \rho)^2/(\rho_0 - 1)^2. \tag{10}$$

Even with the use of these potentials the calculation is extremely complicated, particularly as little earlier work has been carried out on scattering problems associated with spheroids. The differential cross-section corresponding to a definite direction of the axis is found to be expressible in the form

$$I(\alpha, \beta, \phi) = \frac{1}{k^2} \sum_{l, l'} (-1)^{l+l'} \sum_{m, m'=0}^{l, l'} G_l^m(\alpha) G_{l'}^{m'}(\alpha) \sin \eta_l^m \times$$
$$\times \sin \eta_{l'}^{m'} \cos(\eta_l^m - \eta_{l'}^{m'}) \Pi_l^m(\cos\beta)\cos m\phi \, \Pi_{l'}^{m'}(\cos\beta)\cos m'\phi, \tag{11}$$

where α is the angle of incidence, β is the angle of scattering relative to the molecular axis, and the η_l^m are phase parameters depending on

† *Ann. der Physik,* **8** (1930), 521, and **13** (1932), 453.
‡ *Zeits. f. Physik,* **76** (1932), 439.   § Cf. Chap. X, § 5.

V, k, l, and m. The functions $\Pi_l^m(\cos\beta)$ are expressible in series of tesseral harmonics. In order to relate the calculated with observed scattering it is necessary to average the expression (11) over all orientations of the nuclear axis. The scattered intensity is then given by

$$I(\theta) = \frac{1}{k^2}\sum_{l,\,l'}(-1)^{l+l'}\sum_{m,\,m'=0}^{l,\,l'} R_{ll'}^{mm'}(\theta)\sin\eta_l^m\sin\eta_{l'}^{m'}\cos(\eta_l^m-\eta_{l'}^{m'}). \quad (12)$$

$R_{ll'}^{mm'}(\theta)$ is a complicated function of the angle of scattering which is expressed in a series of zonal harmonics by Stier. This formula is to be compared with the formula (17) of Chapter II. The chief difference is that $R_{ll'}^{mm'}(\theta)$ is not just the product of two harmonics but is a sum of several.

Stier carries out the calculation of the functions involved by expansion in powers of ϵ, where

$$\epsilon = (\pi d/\lambda)^2,$$

and his formulae for $R_{ll'}^{mm'}(\theta)$ are only applicable when ϵ is small. To the zero-order approximation (ϵ vanishing) the total cross-section is†

$$Q = \frac{\lambda^2}{2\pi}\sum_l\sum_m(2-\delta_{0m})\sin^2\eta_{lm}, \quad (13)$$

which may be compared with the corresponding expression [Chap. II, (18)], obtained for the scattering by atoms. The only difference is that the phases for different values of m are different.

The numerical application of this formula to the scattering of electrons with less than 10. volts energy by nitrogen has been carried out. With a value of Z of 4·08 and $\rho_0 = 3\cdot46$ the formulae (12) and (13) give very good agreement with experiment. This is illustrated in Fig. 39. The good agreement obtained shows that analysis of results obtained for the scattering of slow electrons by molecules may lead to increased knowledge of the nature of molecular fields.

6. Inelastic Collisions with Molecules. Excitation of Electronic Levels. The Franck-Condon Principle

As is well known, in considering the electronic states of a molecule, one can, to a first approximation, treat the nuclei as though they were at rest; an electronic stationary state exists for any value of the distance between the nuclei. The Franck-Condon principle‡ states that in a transition from one electronic state to another the nuclear distance is instan-

† δ_{0m} is the δ-function, such that $\quad \delta_{0m} = 0 \quad (m \neq 0)$,
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad = 1 \quad (m = 0)$.

‡ Franck, *Trans. Far. Soc.*, **21** (1925), Part 3; Condon, *Phys. Rev.*, **28** (1926), 1192.
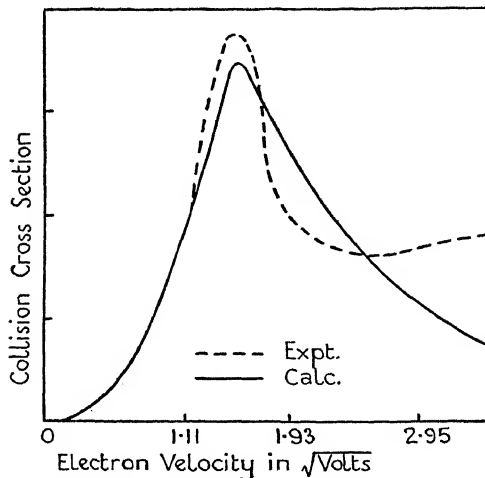
FIG. 39. Comparison of calculated and observed total cross-section curves for nitrogen.

taneously unaltered. Strong experimental evidence in favour of this principle is provided by the measurement of critical potentials of molecules.† It is found in these experiments that excitation of a particular molecular level sets in quite sharply at a given velocity of the exciting electrons, corresponding to the energy necessary to raise the molecule to an excited electronic state with nuclear separation that of the ground state. Thus in Fig. 40, which illustrates the potential energy curves of two electronic states, excitation of the upper state requires energy corresponding to the switch AB, rather than AC.

From the standpoint of classical theory this behaviour is to be expected, owing to the great mass of the nuclei; it is not difficult to see that the quantum theory makes the same predictions, though to a modified extent. Denoting the nuclear separation by ρ, the aggregate of electronic quantum numbers and coordinates by n and $\mathbf{r}$ respectively, and of the nuclear quantum numbers by ν, the probability of transition from a state (n, ν) to a state (n', ν'), due to a certain perturbation, will be proportional to the square of the modulus of

$$\iint F(\mathbf{r}, \rho)\psi_{n\nu}(\mathbf{r}, \rho)\psi_{n'\nu'}^{*}(\mathbf{r}, \rho) \, d\mathbf{r}d\rho, \tag{14}$$

where $F(\mathbf{r}, \rho)$ is the perturbing function producing the transition, and the ψ's are the wave functions of the initial and final states. According

† Whiddington and Jones, *Phil. Mag.*, **6** (1928), 889.
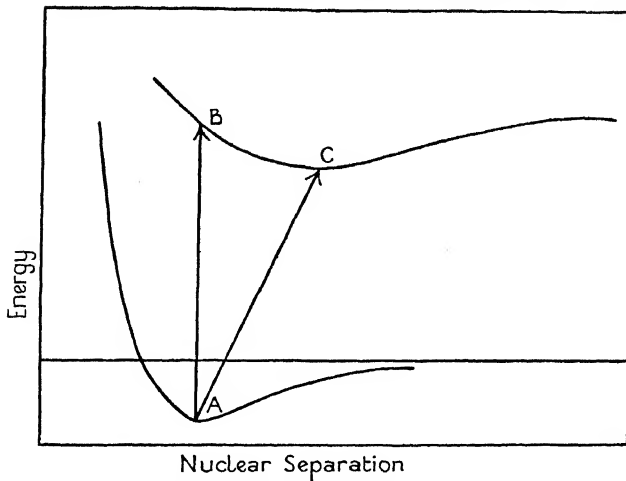
Fig. 40.   Illustrating electronic transitions in a molecule.

to the quantum theory of molecules,† the wave function of a molecule may be written approximately as the product of two wave functions, one $\phi_n(\mathbf{r}, \rho)$ a function of the electron coordinates, and the nuclear separation as parameter, the other $\chi_{n\nu}(\rho)$ of the nuclear coordinates and of the electronic quantum numbers. The function $\psi_{n\nu}(\mathbf{r}, \rho)$ may therefore be written in the form

$$\psi_{n\nu}(\mathbf{r}, \rho) = \phi_n(\mathbf{r}, \rho)\chi_{n\nu}(\rho). \tag{15}$$

Substituting this expression in the integral we may carry out the integration over the electronic coordinates, obtaining an integral over the nuclear coordinates of the form

$$\int G(\rho)\chi_{n\nu}(\rho)\chi_{n'\nu'}^{*}(\rho)\,d\rho. \tag{16}$$

The value of this integral will be determined by the extent to which the wave functions $\chi_{n\nu}$, $\chi_{n'\nu'}$ overlap. These functions, which represent nuclear vibration, assume their largest values in the region where the chance of finding the corresponding classical vibrator is great. Outside the amplitude of the classical motion they tend to zero rapidly as $\rho \to \infty$. Hence the functions $\chi_{n\nu}$ and $\chi_{n'\nu'}$ will only overlap appreciably when the corresponding classical motions overlap, i.e. when the initial and final nuclear separations are nearly the same. As the functions have finite but small values outside the region of classical motion, the integral (16) has a finite value when the Franck-Condon principle is

† Cf. Condon and Morse, *Quantum Mechanics* (1929), Chap. V.

violated. Usually this value will be relatively small, but it may be quite appreciable if the vibrational functions correspond to low quantum states, for in these cases the deviation of the quantum theoretical probabilities from the classical are most pronounced. However, for most purposes the Franck-Condon principle provides a sufficiently accurate description of the behaviour of the nuclei.

7. Diffraction of Inelastically Scattered Electrons by a Molecule†

If we assume the Franck-Condon principle to be strictly valid, the differential cross-section $I_n(\theta)\,d\omega$ corresponding to excitation of a given electronic level is given by

$$I_n(\theta)\,d\omega$$
$$= A\frac{4\pi^2 m^2}{h^4}\frac{k_n}{k}\left|\int\int V(\mathbf{r}_1,\mathbf{r}_2)\psi_0(\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)\exp\{i(k\mathbf{n}_0-k_n\mathbf{n}_1)\cdot\mathbf{r}_1\}\,d\tau_1\,d\tau_2\right|^2 d\omega \tag{17}$$

where ψ_0, ψ_n^* are the electronic wave functions of the initial and final states of the molecule, with nuclear separation that of the *initial* state. The operator A denotes the averaging over all orientations of the nuclear axis; the remaining symbols have their usual significance. Let us now consider the excitation of an electron from a single homopolar bond of a homonuclear diatomic molecule. In this case the wave functions ψ_0, ψ_n may have either the same or opposite symmetry with respect to the nuclear coordinates, and so we may write $\psi_0\psi_n^*$ in the form

$$\psi_0\psi_n^* = f(r,p)\pm f(p,r), \tag{18}$$

where r and p denote coordinates referred to the two nuclei respectively. Denoting the molecular electrons by suffixes 2 and 3, and the incident electron by suffix 1, we have

$$V = \epsilon^2\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}\right)$$

and

$$I_n(\theta)\,d\omega = A\frac{4\pi^2 m^2\epsilon^4}{h^4}\frac{k_n}{k}|J_2+J_3|^2\,d\omega, \tag{19}$$

where

$$J_2 = \int\int\int \frac{1}{r_{12}}[f(r,p)\pm f(p,r)]\exp\{i(k\mathbf{n}_0-k_n\mathbf{n}_1)\cdot\mathbf{R}_1\}\,d\tau_1\,d\tau_2\,d\tau_3,$$

$$J_3 = \int\int\int \frac{1}{r_{13}}[f(r,p)\pm f(p,r)]\exp\{i(k\mathbf{n}_0-k_n\mathbf{n}_1)\cdot\mathbf{R}_1\}\,d\tau_1\,d\tau_2\,d\tau_3. \tag{20}$$

Now one of the functions, say $f(r,p)$, will contain the terms correspond-

† Massey and Mohr, *Proc. Roy. Soc.*, A, **135** (1932), 258.

ing to electron 2 around nucleus 1, and the other, terms corresponding to electron 2 around nucleus 2. It will then be convenient to calculate

$$\int\int\int \frac{1}{r_{12}} f(r,p) \exp\{i(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{R}_1\}\, d\tau_1\, d\tau_2\, d\tau_3 \qquad (21)$$

by changing the origin to nucleus 1, and the other integral by changing to nucleus 2. We then find

$$J_2 = \exp\{\tfrac{1}{2}i(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{d}\} \int\int\int \frac{1}{r_{12}} f(r,p)\exp\{i(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{r}_1\}\, d\tau_1\, d\tau_2\, d\tau_3$$

$$\pm \exp\{-\tfrac{1}{2}i(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{d}\} \int\int\int \frac{1}{r_{12}} f(p,r)\exp\{i(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{p}_1\}\, d\tau_1\, d\tau_2\, d\tau_3, \qquad (22)$$

where $\mathbf{d}$ is the vector distance between the nuclei.

Now $f(r,p)$ can be expanded in the form

$$f(r,p) = \sum_n f_n(r,d) P_n(\cos u),$$

where u is the angle between the radius vector $\mathbf{r}$ and the axis of symmetry of the molecule. Similarly we have

$$f(p,r) = \sum_n f_n(r,d)(-1)^n P_n(\cos u). \qquad (23)$$

If we retain the first term only of these expansions, we find

$$J_2 = \alpha \frac{\cos}{\sin} \{\tfrac{1}{2}(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{d}\}, \qquad (24)$$

according as $\psi_0 \psi_n^*$ is symmetric or antisymmetric in the nuclear co-ordinates. α is a function of k, k_n and θ, but is independent of the angles of orientation. Substituting in the expression (19) for $I_n(\theta)$, we obtain

$$I_n(\theta) = \frac{16\pi^2 m^2 \epsilon^4}{h^4} \frac{k_n}{k} \alpha \frac{\cos}{i\sin} \{\tfrac{1}{2}(k\mathbf{n}_0 - k_n\mathbf{n}_1)\cdot\mathbf{d}\} \; +$$

$$+ \text{higher order oscillating terms.} \qquad (25)$$

Averaging over all orientations of the molecular axis, we then have

$$I_n(\theta) = \frac{8\pi^2 m^2 \epsilon^4}{h^4} \frac{k_n}{k} |\alpha|^2 \left(1 \pm \frac{\sin x}{x}\right) + \text{higher oscillating terms,} \qquad (26)$$

where

$$x = \frac{2\pi d}{\lambda}\left(1 + \frac{\lambda^2}{\lambda_n^2} - 2\frac{\lambda}{\lambda_n}\cos\theta\right)^{\frac{1}{2}},$$

d being the nuclear separation of the initial state.

It is clear from (26) that diffraction effects due to the two nuclei must occur in the excitation of electronic states of molecules by electron collisions. If the initial and final states have opposite symmetries in

the nuclei, this will result in less scattering at small angles, while if the states have the same nuclear symmetry there will be increased scattering at small angles. Such an effect would be difficult to detect experimentally owing to the rapid decrease of $|\alpha|^2$ with increase of angle of scattering, just as for inelastic scattering by atoms. The most favourable conditions would be with low-velocity electrons and heavy molecules.

It is usually stated that waves scattered inelastically from two similar obstacles are incoherent, but this applies only to the intensity of the aggregate of such waves, not to the particular waves which are scattered with a given wave-length change due to excitation of a definite state of the system of obstacles. In the case of a crystal, the states which may be excited lie very close together, owing to the very large number of similar components of the crystal, and it is impossible to resolve the separate inelastically scattered waves. As a consequence no diffraction effects have been observed in the so-called 'incoherently' scattered waves from crystals.

As an example of the above, the probability of excitation of the B-state of molecular hydrogen has been calculated;† for this we refer the reader to the original paper.

8. The Dissociation of Hydrogen Molecules by Electron Impact

As pointed out at the beginning of this chapter, the quantum theory of molecules indicates the possibility of dissociation of molecules by electron impact in a manner unexpected previously. We will illustrate this by reference to hydrogen.

In Fig. 41 the potential energy curves of a number of quantum states of the hydrogen molecule are illustrated, as functions of the nuclear separation. A is the curve for the ground state of the molecule; this is a singlet state (the spins of the two electrons are antiparallel). The minimum at a nuclear separation of 0·75 Å.U. corresponds to the equilibrium state of the molecule. The curves B and C represent in a similar manner the two most important excited singlet states of H_2, the $2^1\Sigma$ and $2^1\Pi$ states. Again, the existence of minima corresponds to a stable equilibrium state. The curve D represents the lowest triplet state of H_2, in which the spins may be parallel or antiparallel. The energy curve has no minimum; the atoms repel one another, and no stable molecule can be formed. The existence of this state was predicted by Heitler and London in 1927.‡ Curves E and F correspond to stable and unstable

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† Massey and Mohr, loc. cit.　　　　　‡ *Zeits. f. Physik,* **44** (1927), 455.

states of the hydrogen molecular ion H_2^+. Above these again would lie the curve corresponding to the doubly ionized molecule H_2^{++}.

To study the energetic relations we consider the molecule as initially in the lowest stable state and in the zero vibrational state, so that the nuclear separation will lie initially in the shaded region in the figure.

Applying the Franck-Condon principle, we see that transitions from the ground state can only take place to states which have finite amplitudes of vibration within the shaded area, corresponding to no change of nuclear separation. A transition from curve A to curve D will result in dissociation of the molecule into two neutral atoms with mutual kinetic energy about 7 volts. Transitions from curve A to curves B or C will result only in excitation and subsequent emission of ultra-violet light, while a transition to E will result in ionization without dissociation. A transition to F will, however, result in dissociation as well as ionization, and the ions produced will have considerable kinetic energy. A summary of these predictions is given in Table I, which includes also certain additional possibilities. The most interesting possibilities are

FIG. 41. Illustrating possible transitions from ground state of hydrogen molecule.

those of dissociation into neutral atoms with mutual kinetic energy, and production of fast positive ions. Both effects have been observed experimentally; the first by Hughes and Skellet,† Glocker, Baxter, and Dalton,‡ and Whiddington and Jones,§ the second by Bleakney.|| Thus all the effects predicted in Table I have been verified, providing direct confirmation of the quantum theory of molecule formation, and the Franck-Condon principle.

These effects occur in many other molecules such as CO, N_2, O_2; for a detailed account of these results the reader is referred to the article

† *Phys. Rev.*, **30** (1927), 11.   ‡ *Journ. Amer. Chem. Soc.*, **49** (1927), 58.
§ *Phil. Mag.*, **6** (1928), 889. || *Phys. Rev.*, **35** (1930), 1180.

TABLE I

Excitation Energy in Volts.	State Excited.	Resulting Transition.	Predicted Effect.
11·0	$1^3\Sigma$	H+H +Kinetic Energy.	High-speed H atoms.
11·5	$2^1\Sigma$	$\rightarrow 1^1\Sigma$	Ultra-violet radiation.
11·8	$2^3\Sigma$	$\rightarrow 1^3\Sigma$	Continuous spectrum.
12·6	$2^1\Pi$	$\rightarrow 1^1\Sigma$	Ultra-violet radiation.
15·6	H_2^+	—	Ionization without dissociation.
18·0	H_2^+ excited above dissociation.	$\rightarrow H^+ + H$	Ionization with dissociation.
28·0 ↓ 40	H_2^+ (unstable).	$\rightarrow H^+ + H$ +Kinetic Energy.	Production of fast H^+ ions.
46 ↓ 56	H_2^{++} (unstable).	$\rightarrow H^+ + H^+$ +Kinetic Energy.	Further production of fast H^+ ions.

The voltages given may be somewhat in error, as the potential energy curves of the higher states are not known with accuracy.

by H. D. Smyth entitled 'Products and Processes of Ionization', in the *Reviews of Modern Physics*, **3** (1931), 348. Unfortunately, the theoretical prediction of the effects cannot be taken further than the calculation of the critical potentials involved. The calculation of relative intensities of the different effects has so far proved too complicated. Massey and Mohr† have considered the probability of dissociation into neutral atoms, using the theory of excitation of triplet states by electron exchange discussed in Chapter XI. They make the approximation of using plane waves and undisturbed molecular wave functions throughout, and so the final results are probably not very accurate. It is found, however, that the maximum probability of the dissociation, which occurs a few volts above the critical potential, is quite large, being comparable with the elastic cross-section. As for all triplet excitations (see Chapter XI), the probability falls off very rapidly with increasing velocity of impact, after first rising to a maximum just beyond the excitation potential. The experiments of Whiddington and Jones,‡ similar to those described in Chap. XI, p. 166, in connexion with inelastic collisions, reveal the existence of a strong 9-volt energy loss for electrons of energies between 14 and 26 volts in hydrogen, which undoubtedly corresponds to this excitation. Their results show that the variation

† *Proc. Roy. Soc.*, A, **135** (1932), 258.   ‡ *Phil. Mag.*, **6** (1928), 889.

of probability with incident voltage is in agreement with theory, but as only non-deviated electrons were observed it is impossible to compare absolute magnitudes.

9. The Excitation of Internal Molecular Motion by Electron Impact

The fact that electrons may interchange energy with nuclear vibration and rotation on impact with molecules is established by a number of experimental investigations.† In particular the experiments of Ramien showed that 2 per cent. of the collisions of 7-volt electrons with hydrogen molecules are inelastic, resulting in excitation of one vibrational quantum.

Such energy exchanges are important in considering the motion of slow electrons through gases, and a satisfactory theory would be thus of considerable interest. For transfer of energy to vibration the theory should follow the same lines as that discussed in Chap. XIII, § 3.5; but it has not yet proved possible to obtain any quantitative results owing to our present inadequate knowledge of the law of force between a vibrating molecule and an electron.

For collisions of electrons with rotating dipoles it can be shown‡ that Born's method is applicable if the dipole moment α is such that

$$\frac{8\pi^2 m\alpha\epsilon}{h^2} \ll 1,$$

m being the mass of the electron. It may then be shown that energy exchange takes place freely on impact, resulting in changes of the rotational quantum number by ± 1. In cases where the law of interaction is more complicated the theory is no longer simple and has not yet been worked out, but it is probable that similar results are to be expected in this case also.

10. The Scattering of Electrons from Crystal Surfaces

The study of the scattering of electrons from crystal surfaces has been of great importance in view of the means afforded of checking de Broglie's formula for the wave-length of electron waves. The famous

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† Bailey, *Phil. Mag.*, **46** (1923), 213, **50** (1925), 825, **13** (1932), 993; Bailey and McGee, *Phil. Mag.*, **6** (1928), 1073; Bailey and Duncanson, *Phil. Mag.*, **10** (1930), 145; Brose and Saayman, *Ann. der Phys.*, **5** (1930), 797; Harries, *Zeits. f. Physik*, **42** (1927), 26; Ramien, *Zeits. f. Physik*, **70** (1931), 353.

‡ Massey, *Proc. Camb. Phil. Soc.*, **28** (1932), 99.

experiments of Davisson and Germer,† G. P. Thomson,‡ and Rupp §
are too well known to need description here.‖

For the diffraction of high-velocity electrons the positions of the
maxima are given by the same formula as for X-rays of the same wave-
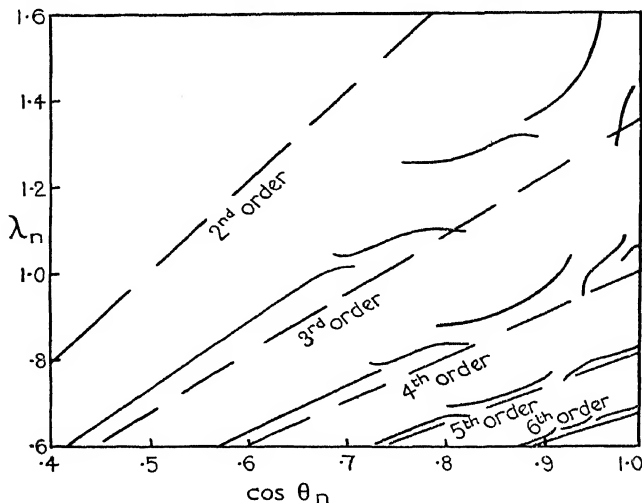
FIG. 42. Values of electronic wave number and angle of incidence of electron beam
for strongly reflected beam.

The crystal is nickel, the surface the 111 plane. Straight broken lines indicate position of analogous
X-ray reflection.

length; the distribution of intensity follows a similar formula; the X-ray
factor $(\epsilon^2/mc^2)F$ must, however, be replaced by††

$$(\epsilon^2/2mv^2)[Z-F]\operatorname{cosec}^2\tfrac{1}{2}\theta.$$

The validity of this formula has been established by several investi-
gators.‡‡

With electrons of energy less than about 1,000 volts it is found that
there are considerable differences between the positions of the maxima
and those for X-rays of the same wave-length. This is illustrated in
Fig. 42, where the wave number for strong reflection is plotted as a
function of the angle of incidence. For X-rays the curves are the
straight lines given by the Bragg formula

$$nd\sin\theta_n = \lambda;$$

† *Phys. Rev.*, **30** (1927), 705.   ‡ *Proc. Roy. Soc.*, A, **117** (1928), 600.
§ *Ann. der Phys.*, **1** (1929), 801.
‖ See, for example, G. P. Thomson, *The Wave Mechanics of Free Electrons*, p. 47,
(1930).   †† Cf. Chap. VII, § 1.   ‡‡ Cf. Chap. IX, § 5.2.

but for slow electrons the lines are not straight. In order to explain these effects, it is necessary to take into account the potential field of the crystal. This has been done by Morse.† He considers the motion of electrons in a periodic field of the form

$$V(x, y, z) = \sum_{l=-\infty}^{\infty} A_{xl} e^{il\alpha x} + \sum_{m=-\infty}^{\infty} A_{ym} e^{im\beta y} + \sum_{n=-\infty}^{\infty} A_{zn} e^{in\gamma z},$$

where A_{xl}, A_{ym}, A_{zn} are constants and α, β, γ are given by

$$\alpha, \beta, \gamma = 2\pi/(d_x, d_y, d_z),$$

the d's being the lengths of the edges of the unit cell of the lattice in the three directions. Using the theory of Hill's equation,‡ he finds that, for an electron beam whose plane of incidence is parallel to the z-axis, the values of the angle of incidence θ_n and wave-number k_n of the incident beam which give regularly reflected beams of maximum intensity, are given by the formula

$$k_n^2 \cos^2\theta_n + \frac{8\pi^2 m}{h^2} V_n = \frac{n^2\pi^2}{d_x^2} + \frac{4\pi^2}{d_y^2} f\{d_x, k_n \sin\theta_n\},$$

where n is an integer and V_n is a quantity which changes very slowly with n and is roughly equal to the mean difference of potential between the interior and exterior of the crystal. The function f is small except near such values of its argument that

$$k_n \sin\theta_n = \pi m/d_y, \tag{27}$$

when it becomes large and discontinuous. As a consequence discontinuities appear, as in Fig. 42, at such angles and directions of incidence that (27) is satisfied. The physical explanation of this effect is that when (27) is satisfied, resonance occurs in the y-direction and nearly all the electrons are reflected back in a direction exactly opposite to that of the incident beam.

For further details the reader is referred to the original papers (loc. cit.).

10.1. *Secondary Electron Emission from Metals.*

A great amount of experimental§ work has been done on this subject, but it is still in a somewhat confused state. Fröhlich‖ has recently considered the problem theoretically by using Born's approximation (Chapter VII). He finds that it is necessary to allow for the deviation of the wave functions of the metal electrons from plane waves

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† *Phys. Rev.*, **35** (1930), 1310. ‡ *Acta Mathematica*, **8** (1886), 1.
§ *Ann. der Phys.*, **13** (1932), 229.
‖ See, for example, Bothe, *Handb. d. Physik*, **24** (1927), 57.

in order to explain the emission. The final results of his calculations show that:

(*a*) There exists a lower limit to the energy of the primary electron in order that secondary emission can take place. This limit is about 15 volts, in agreement with observation.

(*b*) For small velocities of incidence the emission is proportional to $E^{\frac{1}{2}}$, where E is the energy of the primary electron, and for high velocities the emission is proportional to $E^{-\frac{1}{2}} \log(E/W)$, where W is the potential jump at the metal surface.

(*c*) The emission due to primary electrons of 100 volts energy is of the order of magnitude of one secondary electron for each incident primary electron.

THE COLLISIONS BETWEEN MASSIVE PARTICLES

1. Physical Phenomena Involved

BY 'Massive Particles' we mean particles of mass large compared with that of an electron, such as atoms, α-particles, etc. Collisions between such particles may be classified in the following manner.

1.1. *Passage of Fast Massive Particles through Matter*.

Under this heading are included investigations of the ranges of α-particles, fast protons (H-particles), neutrons, and heavy nuclei in various materials. The method of investigation is either by actual observation of single particle tracks in a Wilson Cloud Chamber, or by direct counting of particles by use of scintillations, valve amplification, or other methods. The theoretical problem here is to calculate the energy loss per cm. path through a given material as a function of the mass, energy, and charge of the particles, and the properties of the material. The development of such a theory is important, for observations of energy losses per cm. are often the only means of determining the nature or velocity of the particle.

The question of collisions between nuclei is treated in Chapter XV, § 5.

1.2. *Capture or Loss of Charge on Impact*.

These phenomena are observed both for slow and fast positive ions. The behaviour of α-particles in this respect is discussed in Rutherford, Chadwick, and Ellis's book *Radiations from Radioactive Substances*, 1930, p. 119. Extensive experiments have also been carried out for slower ions, notably by Kallmann and Rosen.[†]

1.3. *Transfer of Excitation*.

This phenomenon is very similar to the transfer of charge mentioned above, consisting in a transfer of electronic or other excitation from one of the colliding systems to the other. It is of considerable importance in experimental physics, particularly in the excitation of spectra. The presence of small quantities of foreign gases often has a very pronounced effect on the intensity, or type, of the spectra produced in a discharge tube. An example is the well-known phenomenon of the quenching of resonance radiation.

The problem here is to evaluate the transition probabilities, particularly as functions of the energy differences of the two excited states.

† *Zeits. f. Physik*, **64** (1930), 808.

1.4. *Elastic Collisions of Gas Atoms.*

The development of molecular ray technique has provided a powerful weapon for the investigation of the interaction of gas atoms. It has proved possible to demonstrate the wave nature of gas atoms by diffraction of beams of helium and hydrogen from crystal surfaces,† and the time is not far distant when investigations of the scattering of atoms by atoms under definite conditions of relative velocity will be a practical possibility. It is therefore of interest to calculate the effects to be expected in the elastic collisions of gas atoms.

The calculation of the collision cross-sections for gas atoms is also of interest in connexion with the theory of viscosity and of other transport phenomena in gases. Thus the variation of viscosity of a gas with temperature depends on the variation of a collision cross-section with relative velocity.‡

1.5. *Mobilities of Positive Ions in Gases.*

A very large number of determinations of the mobilities of ions in gases have been made,§ but it is only in recent years that the experimental conditions have been such as to render possible a clear understanding of the phenomena occurring. However, the recent experiments of Tyndall and others|| have shown that the purity of the gas under investigation is of vital importance. With gases containing even as little as 1 part in 10^6 of impurity, ion clusters are formed, with consequent slowing down of the ion. By high purification of the gases used (argon, helium, and neon) it has been possible to measure the mobilities of cluster-free ions in these gases. As the mobility is determined by the probabilities of collision between the gas atoms and the ions, it is possible to obtain valuable information regarding such collisions from these experiments.

1.6. *Excitation of Inner Molecular Motions.*

Inelastic collisions between molecules, resulting in the excitation of rotation and nuclear vibration, are considered under this heading. At gas-kinetic velocities this is the only possible type of excitation. Direct experimental investigation of these effects, by methods similar to those used for collisions with electrons, is not yet possible; but indirect

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† Cf. Fraser, *Molecular Rays*, 1931, Chap. 4.
‡ See § 3 of this Chapter.
§ Thomson, *Conduction of Electricity through Gases*, 3rd ed., Camb. Univ. Press, 1928.
|| Tyndall and Grindley, *Proc. Roy. Soc.*, A, **110** (1926), 341; Tyndall and Powell, *Proc. Roy. Soc.*, A, **129** (1930), 162; ibid., A, **134** (1931), 125; and ibid., A, **136** (1932), 145. See also Loeb, *Phys. Rev.*, **38** (1932), 549; Bradbury, *Phys. Rev.*, **40** (1932), 508.

evidence as to the probabilities concerned is available from the following sources.

(a) *Measurement of accommodation coefficients.* The thermal accommodation coefficient of gas atoms on a solid surface is determined by the probability of energy exchange between the atoms and the vibrating atoms of the solid. From measurements of accommodation coefficients information may be obtained as to the magnitude of this probability and its variation with temperature.

(b) *The velocity of sound in gases at high temperatures.* An outstanding discrepancy between the theoretical values of the vibrational specific heats of gases, and those measured by velocity of sound methods, has been cleared up by the development of an independent method of measuring the specific heats.† The results obtained by this method agree with theory. The discrepancy is due to the fact that the interchange of energy between vibration and translation is so slow that the gas in a sound wave is not in thermodynamical equilibrium. From the sound measurements it is possible to obtain an estimate of the probability of interchange of vibrational and translational energy.‡

(c) *Reaction rates of unimolecular chemical reactions.* It is an empirical fact that an 'activation' energy is required before a unimolecular reaction will take place. In many cases this consists in the excitation of vibration, and the variation of reaction rate with the pressure of the decomposing gas or of foreign gases yields information as to the probability of activation of vibration by collision. Conversely, a theory of this excitation is of great value in interpreting the observations.

1.7. *Chemical Reactions in General.*

Under this heading are included a vast number of phenomena. The simplest type are two-body collisions, in which a rearrangement of particles takes place on collision; but the most important type are three-body collisions, where combination or dissociation of two molecules takes place under the interaction of a third.

The chief problem here is the calculation of the relative probabilities of different types of reaction in terms of the properties of the reacting substances. A number of extremely general phenomena require explanation, such as catalysis, the nature of activation energy,§ etc.

This classification of the various phenomena, which come under the general title of collisions of heavy particles, is by no means a sharp

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† Blackett, Rideal, and Henry, *Proc. Roy. Soc.*, A, **126** (1930), 319.

‡ Henry, *Nature*, **129** (1932), 200; *Proc. Camb. Phil. Soc.*, **28** (1932), 249.

§ See, however, Polanyi, *Atomic Reactions*, § 1 (1932).

one. The last four processes are of a very similar nature, but as the methods of experimental investigation are very different it was thought best to separate them as above.

Unfortunately the theory of collisions of heavy particles is at present not nearly so well developed as the theory of electronic collisions. Quantitative results are, at present, only available for fast collisions for which Born's first approximation is valid, and for the elastic collisions between gas atoms. However, a number of general results have been obtained for other cases, and for certain problems, such as the excitation of vibration, the only remaining difficulty is the complicated nature of the algebra. Following the same general scheme as for electronic collisions, we consider first the behaviour of fast particles.

2. Fast Collisions of Massive Particles

2.1. *The Stopping-power of Matter for Fast Positive Ions.*

The calculation of the loss of energy per cm. path of fast positive ions traversing matter is very similar to the corresponding calculation for fast electrons, carried out in Chapter XI. We adopt the following notation:

M_1, M_2 are the masses of the colliding and struck systems respectively.

$M = M_1 M_2/(M_1 + M_2)$ is the reduced mass of the combined system.

$Z'\epsilon$ is the charge on the ion.

The symbols k, k_n, κ, $\mathbf{n}_0$, $\mathbf{n}$ have the same meaning as in Chapter XI. The formulae of Chapter XI may be used with the mass of the electron replaced by M, and ϵ^2 by $Z'\epsilon^2$. The differential cross-section in momentum variables is thus†

$$I_{0n}(K)dK = \frac{128\pi^5 M^2 Z'^2\epsilon^4}{k^2 h^4}\frac{dK}{K^3}\,|\epsilon_{0n}(K)|^2,\qquad(1)$$

where

$$\epsilon_{0n}(K) = \sum_{s=1}^{N}\int e^{iKx_s}\psi_0\psi_n^*\,d\tau,$$

and $Kh/2\pi$, as before, is the change of momentum. As before, the effective cross-section corresponding to excitation of the state n will be obtained by integrating the differential cross-section between the limits of allowed momentum change. For the fast collisions under consideration these limits are fixed by the same considerations as for electrons, since the matrix elements $\epsilon_{0n}(K)$ are the same functions of the momentum change $Kh/2\pi$ for both cases.

† Cf. Chap. XI, eq. (10).

The lower limit of K will then be[†]

$$K_{\min} = 4\pi^2 M (E_n - E_0)/h^2;$$

the upper limit is fixed by the conservation of momentum, so that

$$K_{\max} = 2km/(M+m)$$
$$\simeq 2km/M. \tag{2}$$

Apart from these modifications the treatment is exactly the same as for electrons. We obtain the following formulae:

Excitation of optical levels:[‡]

$$Q_{nl,n'l'} = (16\pi^4 Z'^2 \epsilon^4/mv^2)|x_{nl,n'l'}|^2 \zeta_{nl,n'l'} \log\{2mv^2/(E_{n'l'} - E_{nl})\}. \tag{3}$$

Excitation of X-rays:[§]

$$Q^i_{nl} = (2\pi Z'^2 \epsilon^4/mv^2|E_{nl}|) Z_{nl} b_{nl} \log(2mv^2/B_{nl}). \tag{4}$$

Primary ionization:[||]

$$Q_{nl} = (2\pi Z'^2 \epsilon^4 c_{nl} Z_{nl}/mv^2|E_{nl}|)\log(2mv^2/C_{nl}). \tag{5}$$

Energy loss per cm. path:[††]

$$-\frac{dT}{dx} = (4\pi \epsilon^4 Z'^2 N/mv^2) Z \log(2mv^2/E), \tag{6}$$

where $E = 1 \cdot 105 Rh$, for hydrogen.

By comparison with the corresponding formulae for electrons given in Chapter XI in the sections listed below we see that for high-velocity encounters a positive ion of charge $+\epsilon$ behaves in the same way as an electron moving with the same *velocity*. In the case of the energy loss per cm. path, there is a slight difference in the logarithmic term, which is $\log(mv^2/E)$ for an electron, but $\log(2mv^2/E)$ for a massive particle.

The accuracy of these expressions, as representing the observations, has been considered by Blackett[‡‡] and by E. J. Williams.[§§] In Table I a comparison of observed and calculated values for the energy loss per cm. of α-particles passing through certain gases is given. u is the velocity of the incident particle, v of the electron in the atom.

The agreement appears to be quite satisfactory, except for oxygen. Referring to (6) it will be seen that the calculation of the stopping-power requires a knowledge of the mean excitation energy E of the atom concerned. For an atom such as oxygen it is difficult to obtain this accurately; the value assumed in obtaining the figures given in Table I have been obtained using formula (70) and Table V of Chapter XI. A further source of error may arise from the inaccuracy

[†] Cf. Chap. XI, § 1.1.   [‡] Cf. Chap. XI, § 3.1.   [§] Cf. Chap. XI, § 3.2.
[||] Cf. Chap. XI, § 3.3.   [††] Cf. Chap. XI, § 4.2.
[‡‡] *Proc. Roy. Soc.*, A, **135** (1932), 132.   [§§] Ibid. 108.

TABLE I

Gas.	u^2/v^2.	$\left(\dfrac{dT}{dx}\right)\Big/(2\pi N Z Z'^2 \epsilon^4/mv^2)$.	
		Observed.	Calculated.
H_2	0·01	11·1	10·9
H_2	0·02	9·3	9·9
O_2	0·01 → 0·5	7·5	9·4

of Born's approximation for collisions of the relatively slow α-particles with an atom in which the orbital velocity of the K electrons is quite high.

Using formula (6), we find that a particle passing through a gas containing N atoms per c.c. will, in losing velocity from v_1 to v_2, move a distance R given by

$$R = (ME^2/32\pi\epsilon^4 Z'^2 ZmN)[Ei(y_2) - Ei(y_1)], \tag{7}$$

where Z is the nuclear charge of the atoms through which the particle is passing, and

$$y_1 = 2\log(2mv_1^2/E), \qquad y_2 = 2\log(2mv_2^2/E),$$

$$Ei(y) = \int^{y} e^{-x}x^{-1}\,dx,$$

Blackett† has discussed the experimental evidence with reference to this expression, and has shown that for gases such as air, the formula (7) will fit the experimental results for α-particles and fast protons very well if the mean excitation energy E is suitably adjusted. For air a value of E of 127 electron volts is found to fit the results best.

2.2. *The Capture of Electrons by Fast Positive Ions.*

(a) *Bound electrons.* In most experimental investigations the main capture process consists in the extraction of a bound electron from an atom by the positive ion; we shall consider this process first.

The general theory necessary has been developed in Chapter VIII, this being a rearrangement collision in which the reaction is

(Nucleus A and electron)+Nucleus B

$\to$ Nucleus A+(Nucleus B and electron).
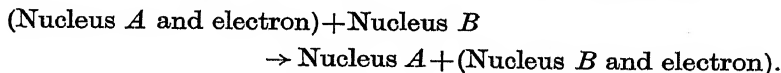
Since we are dealing with fast collisions we may use Born's approximation and the formulae of Chapter VIII, § 4.2. The cross-sections for capture of an electron from state n around nucleus A to state q around

† Loc. cit.

nucleus B is given from Chap. VIII, eq. (68) by

$$Q_{nA \to qB}$$
$$\frac{k_q}{k} \frac{8\pi^3 M^2}{h^4} \int_0^\pi \left| \int \int V(\mathbf{r}_e, \boldsymbol{\rho}) \phi_q^*(\mathbf{r}_e) \psi_n(\mathbf{r}_e) \exp\{i(k\mathbf{n}_0 \cdot \mathbf{r} - k_q \mathbf{n} \cdot \boldsymbol{\rho})\} d\mathbf{r}_e d\boldsymbol{\rho} \right|^2 \sin\theta \, d\theta.$$

$$(8)$$

Here $V(\mathbf{r}_e, \boldsymbol{\rho})$ is the interaction energy between the nucleus A and the electron, $\psi_n(\mathbf{r}_e)$ is the wave function of the electron in the state n round nucleus A, $\phi_q(\mathbf{r}_e)$ is that of the same electron in the state q around nucleus B, $\boldsymbol{\rho}$ is the distance between the nucleus A and the centre of mass of the system (nucleus B+electron), and $\mathbf{r}_e$ denotes the electronic coordinates. M is the reduced mass of the final system; if we denote the masses of the nuclei A and B by M_A, M_B respectively and the mass of the electron by m, then

$$M = M_A(M_B + m)/(M_A + M_B + m).$$

The wave numbers k, k_q are given by

$$k = \frac{2\pi v}{h} \frac{(M_A + m)M_B}{M_A + M_B + m}, \qquad k_q = \frac{2\pi v'}{h} \frac{(M_B + m)M_A}{M_A + M_B + m}, \qquad (9)$$

v, v' being the initial and final relative velocities. $\mathbf{n}_0$, $\mathbf{n}$ denote unit vectors in the directions of initial and final relative motion, so that $\mathbf{n}_0 \cdot \mathbf{n} = \cos\theta$.

It is convenient to evaluate (8) by changing from the coordinates $\boldsymbol{\rho}$, $\mathbf{r}_e$ to the coordinates $\mathbf{r}_A$, $\mathbf{r}_B$ which denote the positions of the electron relative to the nuclei A, B respectively. We then obtain

$$Q_{nA \to qB} = \frac{k_q}{k} \frac{8\pi^3 M^2}{h^4} \int_0^\pi \left| \int \int V(r_A) \phi_q^*(\mathbf{r}_B) \psi_n(\mathbf{r}_A) \times \right.$$
$$\left. \times \exp\left\{ \frac{2\pi i}{h} (\mathbf{A} \cdot \mathbf{r}_A - \mathbf{B} \cdot \mathbf{r}_B) \right\} d\mathbf{r}_A d\mathbf{r}_B \right|^2 \sin\theta \, d\theta, \quad (10)$$

where $V(r_A)$ is written for $V(\mathbf{r}_e, \boldsymbol{\rho})$, and

$$(M_A + M_B + m)\mathbf{A} = M_A M_B v \mathbf{n}_0 - M_A(M_B + m)v' \mathbf{n}$$
$$(M_A + M_B + m)\mathbf{B} = M_B(M_A + m)v \mathbf{n}_0 - M_A M_B v' \mathbf{n}. \qquad (11)$$

Since the variables occurring in the double integrals are now separable, the calculation may be completed without difficulty if the atomic wave functions have a simple form.

The calculation of the cross-section $Q_{nA \to qB}$ for capture into a $1S$ state from a $1S$ state has been carried out by Brinkmann and Kramers

using formula (10).† They find that if the velocity v is so high that the contribution to the cross-section comes only from small momentum changes,

$$Q = \tfrac{1}{5}2^{18}\pi a_0^2 Z^5 Z'^5 s^8 [s^2 + (Z+Z')^2]^{-5}[s^2 + (Z-Z')^2]^{-5}, \qquad (12)$$

where $s = hv/2\pi\epsilon^2$ and Ze, $Z'e$ are the nuclear charges. This expression
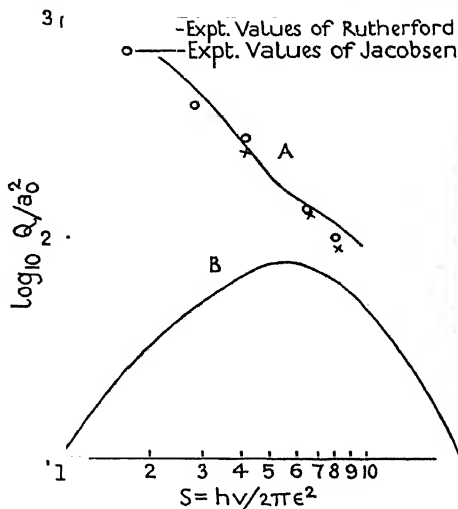
FIG. 43. Cross-sections for capture of electrons
by α-particles.
A. Theoretical curve for nitrogen.
B. Theoretical curve for capture into a $1S$ state from a
nucleus of charge 7.

shows that for high velocities the probability of capture falls off as v^{-12}, in sharp contrast to the excitation probability which, for optically allowed transitions, falls somewhat more slowly than v^{-2} (see formula (3) of this chapter). This is due to the presence in the capture problem of a term proportional to v in the minimum momentum change, due to the momentum involved in the electron transfer. No such term occurs in the case of direct excitation.

Since the experiments of Rutherford‡ and of Jacobsen§ refer to the capture of electrons by α-particles moving through air, Brinkmann and Kramers (loc. cit.) carried out the calculations approximately for capture from nitrogen atoms. They obtained reasonably good agreement with experiment, as is shown in Fig. 43. The empirical law found by

† K. Wet. Amst., 33 (1930), 973.   ‡ Phil. Mag., 47 (1924), 277.
§ Ibid. 10 (1930), 401.

Rutherford to represent the variation of the probability of capture with velocity, namely,

$$Q \propto v^{-5\cdot6}, \tag{13}$$

is due to the fact that in the experimental range the probability of capture of a K electron increases with increasing velocity of the α-particle, whereas the cross-section for capture of an L electron decreases with nearly the 12th power of the velocity. The combination of the two effects leads to the law (13).

The effect of capture and loss of electrons on the rate of loss of energy of fast positive ions traversing matter has not been investigated theoretically, but the importance of capture in this phenomenon has been emphasized by Blackett.†

(*b*) *Free electrons.* The capture of a free electron by an ion may be considered as a spontaneous transition of the electron from a state of the continuous spectrum of the neutral atom to a discrete state of the same atom. It differs from the previous case in that the excess energy is not taken up as energy of relative translation but is liberated as radiation.

According to the theory of spontaneous emission of radiation, if a beam of electrons falls on an atom, the number of transitions per second producing light of frequency ν_n polarized in the x direction, is given in terms of the cross-section Q_κ^{nlm}, where

$$Q_\kappa^{nlm} = \tfrac{1}{3}64\pi^4(\nu_n/c)^3\epsilon|X_{\kappa,nlm}|^2/h.$$

$X_{\kappa,nlm}$ is the matrix element

$$\int \psi_\kappa x\psi_{nlm}^* \, d\tau,$$

ψ_κ being the initial wave function (that of the continuous spectrum normalized as in Chap. XIV, § 2) and ψ_{nlm} the final wave function. The evaluation of these cross-sections corresponding to capture of free electrons by hydrogen-like atoms has been carried out by Stueckelberg and Morse‡ and by Wessel.§

3. Slow Collisions of Heavy Particles

3.1. *Elastic Collisions of Gas Atoms.*

As was pointed out in § 1.4 of this chapter, it is of considerable interest to calculate the collision cross-sections for gas atoms colliding with each other with gas-kinetic velocities. Besides the total elastic cross-section Q, which may now be measured directly by molecular ray

† *Proc. Roy. Soc.*, A, **135** (1932), 132.   ‡ *Phys. Rev.*, **36** (1930), 16.
§ *Ann. der Phys.*, **5** (1930), 611.

methods,† we require also the cross-sections Q_η, Q_D which are effective in viscosity and diffusion respectively. These are defined by‡

$$Q_\eta = 2\pi \int_0^\pi I(\theta)\sin^3\theta \, d\theta$$

$$Q_D = 2\pi \int_0^\pi I(\theta)\sin^2\tfrac{1}{2}\theta \sin\theta \, d\theta,$$

(14)

where $I(\theta)$ is the scattered intensity in relative coordinates. These may be compared with

$$Q = 2\pi \int_0^\pi I(\theta)\sin\theta \, d\theta$$

(15)

[cf. Chap. II, eq. (18)].

The coefficient of viscosity η of a simple gas at absolute temperature T is then given by§

$$\eta = \frac{5}{4j^3M^2}\left(\frac{2\pi}{jM}\right)^{\frac{3}{2}}\frac{1+\epsilon}{\pi R_{11}},$$

where $j = 1/2\kappa T$, M is the mass of a gas atom, κ is Boltzmann's constant, and R_{11} is given by

$$R_{11} = \tfrac{1}{2}\int_{-\infty}^\infty v^7 Q_\eta e^{-\frac{1}{2}jMv^2} \, dv;$$

v denotes the relative velocity of the gas atoms, of which Q_η as defined above is a function; ϵ is a small correcting term of order 10^{-2}.

Further, the coefficient of diffusion D between two gases (distinguished by suffixes 1 and 2) is given by

$$D = \tfrac{3}{16}\pi^{\frac{1}{2}}\left(\frac{M_1+M_2}{jM_1M_2}\right)^{\frac{7}{2}}\frac{1}{(\nu_1+\nu_2)P_{12}}\frac{1}{1-\epsilon_0},$$

where ν_1, ν_2 denote the numbers of each kind of atom per unit volume, M_1, M_2 are the masses of each kind of gas atom, ϵ_0 is a small correcting term‖ depending on ν_1, ν_2, and

$$P_{12} = 2\int_{-\infty}^\infty v^5 Q_D \exp\left[-\frac{jM_1M_2}{M_1+M_2}v^2\right] dv.$$

In order to investigate the modifications of the classical formulae which are introduced by the quantum theory it is simplest to start

† Cf. Fraser, *Molecular Rays*, 1931, Chap. 4.
‡ Vide Massey and Mohr, *Proc. Roy. Soc.*, A, in press.
§ Chapman, *Phil. Trans.*, A, **216** (1916), 279; **217** (1917), 115. See also Massey and Mohr, loc. cit.
‖ Chapman, *Phil. Trans.*, A, **217** (1917), 115.

with the rigid sphere model for the gas atoms. We thus set for the interaction energy between the spheres

$$V(r) = \infty \qquad (r < r_0)$$
$$= 0 \qquad (r > r_0).$$

On the classical theory this gives for Q the value πr_0^2 and for $I(\theta)$ the value $\tfrac{1}{4}r_0^2$. To calculate the scattering on the quantum theory the method of Chapter II may be applied (cf. Chap. II, § 3.2, where it is shown that in the low-velocity limit $Q \rightarrow 4\pi r_0^2$). If the colliding atoms
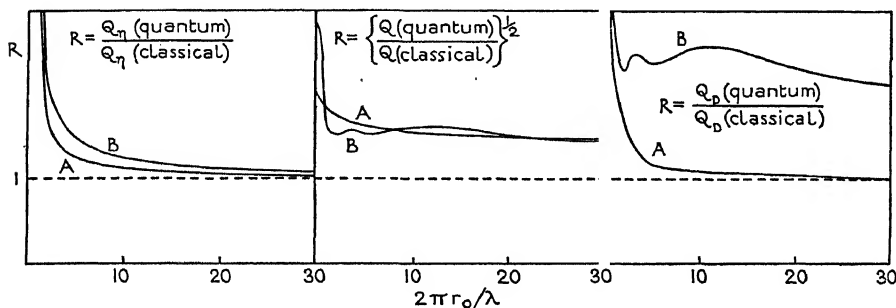
Fig. 44. Illustrating behaviour of quantum theoretical cross-sections effective in viscosity, scattering, and diffusion, on the hard sphere model.
Curves A refer to dissimilar atoms, B to identical atoms.

are similar, account must also be taken of the symmetry relations introduced by the Bose-Einstein statistics (cf. Chap. V). In this case $I(\theta)$ contains only even harmonics and so is symmetrical about $\theta = \tfrac{1}{2}\pi$. The exclusion of odd harmonics has the general effect of increasing the deviations from classical theory, as will be observed from Fig. 44, in which the quantum and classical values of Q, Q_η, and Q_D are compared.

We note that, although the cross-sections Q_η and Q_D tend to the classical values as the ratio of wave-length to atomic diameter is decreased, the total cross-section Q tends, not to its classical value, but to twice that value. The reason for this different behaviour will be clear by reference to Fig. 45, which illustrates the calculated angular distribution function $I(\theta)$. It will be seen that $I(\theta)$ differs from the classical value only at small angles of scattering. The angle at which the deviations first become apparent decreases with decrease of wavelength, but the magnitude of the deviation within this angular range *increases* with decrease of wave-length in such a way that Q remains twice the classical value. Q_η and Q_D, however, differ from Q in that

their magnitude depends mainly on large angle collisions. For such collisions classical mechanics becomes valid when the wave-length is sufficiently short. Classical and quantum theories *never* give the same result for *all* angles; there remains always a small angular range at which they differ (cf. Chap. VII, § 3).
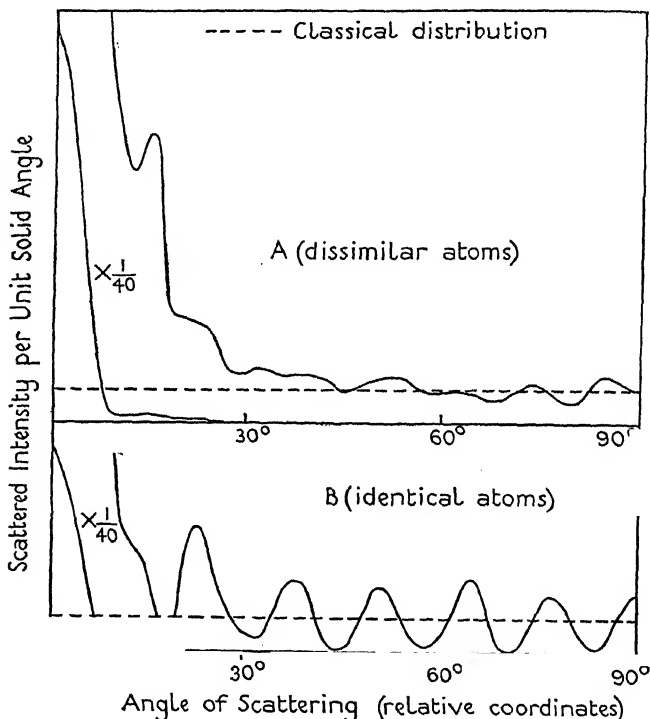
FIG. 45. Angular distributions of scattered atoms on the rigid sphere model for $2\pi r_0/\lambda = 20$.

As a result of the quantum modifications of Q_η for helium atoms the hard sphere model is found to represent the variation of the viscosity of helium with temperature, over the range from 25° K. to 300° K. within 7 per cent. This is of special interest in view of the fact that the deviations observed in this range from the law given by the classical rigid sphere model have been used to determine the law of force between helium atoms.† It is clear therefore that quantum formulae must be used in calculating the viscosity of such light gases as helium and

† Cf. R. H. Fowler, *Statistical Mechanics*, Chap. X (contributed by J. E. Lennard-Jones).

hydrogen even at ordinary temperatures. In order to calculate cross-sections for complicated fields of force, it is necessary to evaluate a large number of phases; to do this by numerical integration of the corresponding differential equations would be extremely laborious. This difficulty may be overcome by using Jeffreys'† method to evaluate those phases greater than unity and Born's approximation‡ for those considerably less than unity, the intermediate phases being obtained by interpolation on a phase-order diagram. This method has been applied§ using the field of interaction between helium atoms given by Slater and Kirkwood.||

In the past, viscosity and, to a lesser extent, diffusion phenomena in gases have been used as a means of determining the laws of force between gas atoms. The use of quantum theory shows that a further method may be used, for the total elastic cross-section Q (which has no meaning on classical theory, cf. Chap. II, § 1; Chap. X, § 1) depends also on the field of force between the colliding atoms and, since it is more sensitive to changes in the number of small angle collisions than either Q_η or Q_D [see formulae (14) and (15)], it depends more on the interaction energy at large distances. The measurement of Q as a function of temperature therefore enables us, in principle, to determine the field of force between the atoms concerned. The introduction of molecular ray methods has made the range of practical applicability of this method much greater than the two earlier ones mentioned above. Q has been calculated for a number of possible fields of force by Massey and Mohr and the use of their formulae in connexion with experimental observations of total collision areas should lead to considerable further knowledge of atomic interactions.

The form of the angular distribution of the scattered atoms is of interest in molecular ray work, both for its own sake and to enable estimates to be made of the angular resolution required for the accurate measurement of free paths. The latter question has been discussed by Massey and Mohr (loc. cit.) who give a method for determining the resolution necessary in any particular case. With regard to the possibility of detecting experimentally the maxima and minima exhibited in Fig. 45, it is clear that, for the collision of dissimilar atoms, the Maxwellian distribution of velocities in the colliding beams will smooth out the angular distributions. For similar atoms, on the other hand, the maximum at 90° (45° when one atom is initially at rest) is present at

all velocities of impact, and so should be detectable even with non-monochromatic beams. In this way it may be possible to establish directly the validity of the Bose-Einstein statistics to which the maximum is due.

Similar considerations may be applied to the motion of slow positive ions in gases.

3.2. *The Transfer of Excitation.*

The importance of the transfer of excitation between atoms on collision has already been mentioned at the beginning of this chapter. The general feature which emerges from the experimental data is that the probability of this transfer is a maximum when the energy difference between the two states is zero. The energy difference appears to be usually more important in determining the probability of the transfer than the relative velocities or nature of the systems concerned. As an illustration of this we shall consider the results of a few selected experiments.

3.21. *Quenching of Mercury Resonance Radiation.*

It is well known that the presence of a foreign gas in a mercury resonance lamp has the effect of diminishing the intensity of resonance radiation. This is due to the deactivation of the excited mercury atoms by collision with molecules of the foreign gas. From observations of the variation in intensity of the resonance radiation with different foreign gases present it is possible to determine the effective cross-sections corresponding to deactivation of the mercury atoms by the gas molecules. Such a series of observations was carried out by Zemansky;[†] in Fig. 46 the relative efficiencies of different gases in producing the transition $2\,^3P_1 \rightarrow 2\,^3P_0$ of the mercury atom, which requires 0·218 volts, are illustrated. The efficiency is given in terms of the effective cross-section, and is plotted against the energy of the vibrational level of each gas with energy nearest to the resonance value 0·218 volts. It is clear that the points obtained determine a resonance curve of the usual type. Carbon monoxide alone behaves anomalously, showing that the energy difference is not the only factor concerned.

3.22. *The Absorption of Positive Ions. 'Umladung.'*

The observed absorption of slow positive ion beams in gases is due almost entirely to neutralization, by capture of electrons from the gas molecules. A large number of measurements of the absorption coefficients of ions in gases have been carried out by various investigators, and in all cases

† *Phys. Rev.*, **36** (1930), 919.

the absorption coefficient of a gas is found to be greatest for ions of the same gas; that is to say, positive ions are absorbed most strongly by gases which form the same ions by loss of an electron. Thus N^+ ions are absorbed less strongly than N_2^+ ions in nitrogen,[†] and H_2^+ ions are
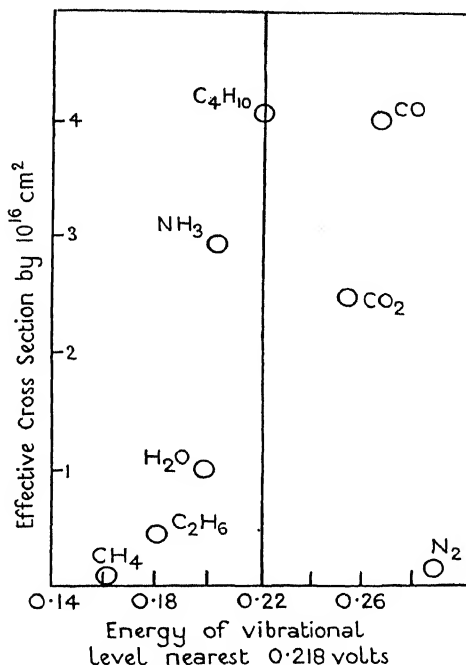
FIG. 46. Illustrating relative efficiencies of various gases in quenching mercury resonance radiation.

absorbed more strongly in H_2 than either H^+ or H_3^+, despite the large size of the triatomic ion.[‡]

3.23. *Excitation of Sodium by Excited Mercury Atoms.* Experiments of a somewhat similar nature were carried out by Beutler and Josephy,[§] who irradiated a mixture of sodium and mercury vapours with a mercury lamp and measured the intensity of the sodium lines with excitation energies in the neighbourhood of that of the exciting line (wavenumber 2537). Allowing for the statistical weight of the terms involved

† Kallmann and Rosen, *Zeits. f. Physik*, **64** (1930), 808.
‡ Holzer, *Phys. Rev.*, **36** (1930), 1204.
§ *Zeits. f. Physik*, **53** (1929), 755.

in the sodium lines, they obtained the curve illustrated in Fig. 47 for the excitation probability of the different sodium levels represented as a function of the energy of the level. A strong maximum is observed at the resonance point with a subsidiary maximum corresponding to resonance with the metastable $2\,^3P_0$ state of mercury.
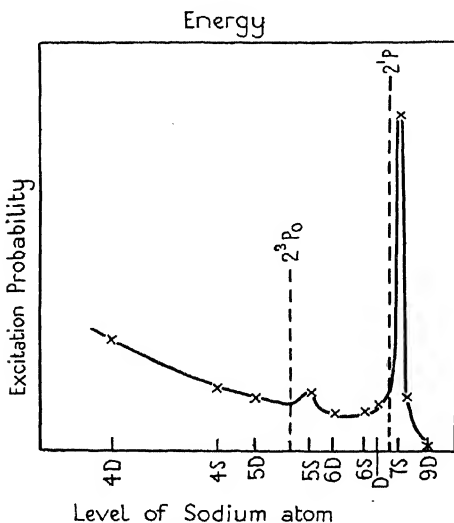
FIG. 47. Excitation probabilities of various sodium lines by collisions of the second kind with mercury atoms excited to the 2^1P state.

Dotted lines indicate energies of the 2^1P and 2^3P_0 states of mercury.

A great number of other examples of this phenomenon are known,† and it is clearly of great importance in chemical kinetics. Thus a molecule is much more effective than an atom in deactivation, as it can take up energy by change of rotation quantum number, whereas an atom can only do so by change of kinetic energy.

We now consider these phenomena from a theoretical point of view.

3.3. Theory of Resonance Effects.

In Chapter VIII, § 3.2, a method of calculation of cross-sections for transitions between two states in approximate resonance was discussed. We use the same notation in this section, and denote the initial state by the suffix 0 and the final state by the suffix n. In the two following cases it was shown that the problem consists in the solution of two simultaneous differential equations only. If the states 0 and n are in approximate resonance, or if the interaction energy terms V_{st} are small for all states s and t, the probability of the transition is determined by a function F_n which is a solution of the simultaneous equations

$$\left\{\nabla^2 + k^2 - \frac{8\pi^2 M}{\hbar^2} V_{00}\right\} F_0 = \frac{8\pi^2 M}{\hbar^2} V_{0n} F_n$$

$$\left\{\nabla^2 + k_n^2 - \frac{8\pi^2 M}{\hbar^2} V_{nn}\right\} F_n = \frac{8\pi^2 M}{\hbar^2} V_{0n} F_0. \tag{16}$$

† Cf. Franck and Jordan, *Anregung von Quantensprüngen durch Stösse*, 1926, p. 216; Ruark and Urey, *Atoms, Molecules, and Quanta*, 1930, Chap. XIV.

F_0 represents the incident and elastically scattered wave, and must have the asymptotic form

$$F_0 \sim e^{ikz} + r^{-1}e^{ikr}f(\theta, \phi). \tag{17}$$

F_n represents an outgoing wave, so that

$$F_n \sim r^{-1}e^{ik_n r}f_n(\theta, \phi).$$

The cross-section corresponding to the transition $0 \to n$ will then be

$$Q_n = \frac{k_n}{k} \int_0^\pi \int_0^{2\pi} |f_n(\theta, \phi)|^2 \sin\theta \, d\theta d\phi.$$

In the case when V_{st} is small for all s and t, the term in V_{0n} can be taken as a perturbation and the equations (16) solved by successive approximations, as in Chapter VIII, § 3.2. It is then found that

$$f_n(\theta, \phi) = -\frac{2\pi M}{h^2} \int V_{0n}(r')F_0(r', \theta')\mathfrak{F}_n(r', \pi-\Theta) \, d\tau', \tag{18}$$

where $F_0(r, \theta)$, $\mathfrak{F}_n(r, \theta)$ are solutions, both with asymptotic form similar to (17), of

$$\{\nabla^2 + k^2 - (8\pi^2 M/h^2)V_{00}\}F_0 = 0 \tag{19}$$

and

$$\{\nabla^2 + k_n^2 - (8\pi^2 M/h^2)V_{nn}\}\mathfrak{F}_n = 0. \tag{20}$$

Θ denotes the angle between the directions θ, ϕ and θ', ϕ'. This method is described in Chapter VIII under the heading of 'Method of Distorted Waves'.

The formula (18) has been applied by Morse and Stueckelberg† to a great many phenomena, with a view to investigating the variation of the cross-section with the 'Resonanz-Unschärfe' (the energy difference between the initial and final states). For the collisions of atoms it has not as yet been possible to make accurate calculations of any of the quantities involved in the integrand of (18); but it is possible to choose forms which represent the behaviour of the systems fairly accurately, and which enable the equations (19) and (20) to be solved in terms of known functions. Thus Morse and Stueckelberg took for V_{00} and V_{nn} the forms

$$V_{00} = \alpha_0/r^2 \qquad V_{nn} = \alpha_n/r^2$$

The constants α_0, α_n were adjusted so that, with velocities corresponding to the temperature of the gas involved, the closest distance of approach of the two atoms was equal to the sum of their gas-kinetic radii. The equations (19) and (20) were solved in series of Bessel functions. Various

† *Ann. der Phys.*, **9** (1931), 579.

forms were taken for $V_{0n}(r)$. If the transitions in both systems A and B are optically allowed, they take asymptotically for large r

$$V_{0n}(r) \sim a_2/r^2,$$

where a_2 is a constant. If one transition is allowed while the other has only a quadrupole moment, they take

$$V_{0n}(r) \sim a_3/r^3,$$

and if both are associated with quadrupole moments

$$V_{0n}(r) \sim a_4/r^4.$$

Finally, if either transition is associated with no moment, they take

$$V_{0n}(r) \sim a_5 e^{-\lambda r}.$$

Such a transition may occur with electron exchange or with $S \to S$ transitions.

For all atoms the functions V_{00} and V_{nn} represent strongly repulsive fields; thus the wave functions F_0, $\mathfrak{F}_n$ have no appreciable magnitude for distances much less than the classical distance of closest approach. As a consequence, the asymptotic expressions given above for V_{0n} are sufficiently accurate. The remaining calculation consisted then in summing series of integrals involving Bessel functions. The results of the calculations are illustrated in Fig. 48. The quantity β is related to the sum d_0 of the gas-kinetic radii of the reacting atoms by the expression

$$\beta = 2 \cdot 2 (d_0/a_0) M^{\frac{1}{2}},$$

where M is the reduced mass of the system in terms of the mass of the hydrogen atom. In the case of dipole-dipole and dipole-quadrupole transitions the dependence of the cross-section on velocity takes the form

$$Q_{0n} \propto \phi(\Delta E/E)$$

and

$$Q_{0n} \propto E\phi(\Delta E/E), \tag{21}$$

where ΔE is the energy difference between the two states (the 'Resonanz-Unschärfe'); the functions ϕ are illustrated for different values of β.

For interaction terms vanishing exponentially the dependence of Q on E and ΔE is not so simple and must be written in the form

$$Q_{0n} \propto \chi(E)\,\phi[(\Delta E/E), E]. \tag{22}$$

The functions $\chi(E)$, $\phi[(\Delta E/E), E]$ are illustrated separately in Fig. 48 c.

In all cases we note that the function ϕ is of the exact form found experimentally (Figs. 46, 47). The resonance is particularly sharp for optically allowed transitions and large atoms (large β).

It remains to consider the transfer of charge. For this case the interaction term is of the form

$$V_{0n} \sim (\epsilon^2/a_0)e^{-r/r_0},$$

where r_0 is between 2 and 4 times a_0. In this case, again, the cross-

$$V_{0n} \sim a_2/r^2$$
$$Q = c\phi(\Delta E/E).$$
(a)

$$V_{0n} \sim a_3/r^3$$
$$Q = cE\phi(\Delta E/E).$$
(b)

$$Q = c\chi(E)\phi(\Delta E/E)$$
$$\alpha = M(r_0/a_0)^2 E.$$
(c)
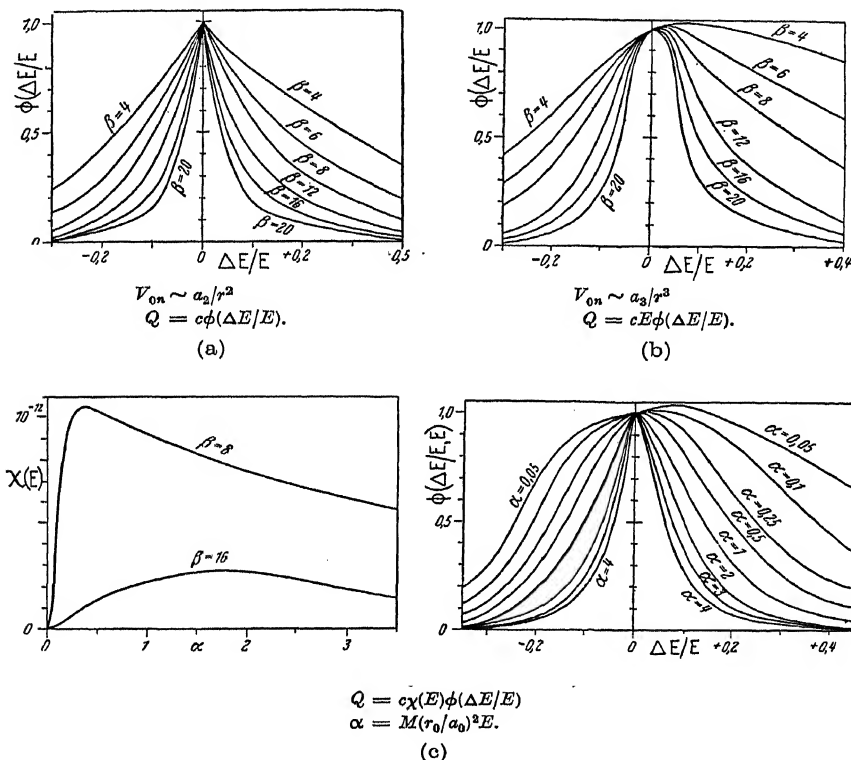
Fig. 48.   Calculated cross-sections for transfer of excitation.

section Q takes the form (22). The forms of the functions χ and ϕ are illustrated in Fig. 49 a, again establishing the resonance nature of the phenomenon. Fig. 49 b illustrates the variation of the cross-section with velocity for various fixed values of ΔE. The form of these curves is in agreement with the experiments of Bartels,† who has measured the mean free paths of slow protons in molecular hydrogen, but the calculated maximum occurs at too low a voltage. This defect is probably due to the failure of the approximations when the interaction is large.

† *Ann. der Phys.*, **13** (1932), 373.

However, it is clear that for small interactions the method is successful in explaining the observations. The resonance effect is mainly due, according to the theory outlined above, to the fact that the product of the incoming and outgoing waves in formula (18) makes a large con-

(a)

(b)

$$V_{0n} \sim (e^2/a_0)e^{-r/r_0}$$
$$Q : : c\chi(E)\phi(\Delta E/E, E)$$
$$\omega : : M(r_0/a_0)^2 \Delta E.$$
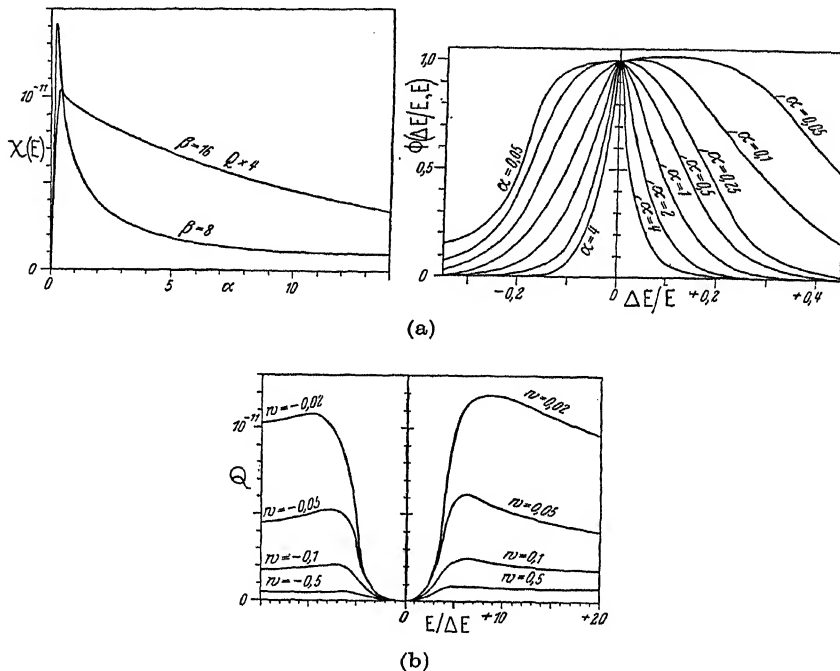
FIG. 49. Calculated cross-sections for charge transfer.

tribution to the integral when the wave-lengths are nearly equal. The matrix element V_{0n} is also probably greater in the resonance case.

3.31. *The Case of Strong Interaction.* To extend the theory further it is necessary to develop accurate approximate methods for the solution of the simultaneous equations (16) when V_{0n} can no longer be considered small. Such methods have been introduced by London[†] and by Stueckelberg.[‡]

London's method is derived from a consideration of the physical

† *Zeits. f. Physik*, **74** (1932), 143.　　　　‡ *Helv. Phys. Acta*, **5** (1932), 370.

nature of the processes occurring. When the interaction V_{0n} is large the perturbation method fails owing to the occurrence of adiabatic phenomena. As the interacting systems approach and separate again transitions occur in both directions. Morse and Stueckelberg's method does not allow for the reverse process occurring before the systems separate, and so gives too large a probability.† London therefore bases his approximations, not on stationary state wave functions which are unperturbed by the interaction, but on wave functions which are nonstationary in that they include the adiabatic energy changes. The method then follows on the same lines as that described in Chap. VIII, § 3.3, as the Method of Perturbed Stationary State Wave Functions. In this way London arrives at a formula which differs from (18) in that the interaction energy V_{0n} is replaced by

$$\tfrac{1}{2}(E_0 - E_n)\arctan[2V_{0n}/\{E_0 - E_n + V_{00} - V_{nn}\}]. \tag{23}$$

To obtain a more accurate solution of (16), it is necessary to expand the functions F_0, F_n in series of spherical harmonics, and to adapt the method of Chap. II, § 1, to the problem under consideration. We thus set

$$F_0 = \sum_s F_0^s P_s(\cos\theta), \qquad F_n = \sum_s F_n^s P_s(\cos\theta). \tag{24}$$

The functions F^s must be found, subject to the boundary conditions that F_0 must represent an incident wave, and F_n a scattered wave, so that the functions F^s have asymptotic form, for large r,

$$F_0^s \sim (2ikr)^{-1}(2s+1)\exp(i\eta_0^s)i^s \times$$
$$\times [\sin(kr - \tfrac{1}{2}s\pi + \eta_0^s) + q_0^s \exp\{i(kr - \tfrac{1}{2}s\pi + \eta_0^s)\}]$$
$$F_n^s \sim (2ikr)^{-1}(2s+1)q_n^s i^s \exp\{ikr + 2i\eta_n^s\}, \tag{25}$$

where q_n^s, η_n^s, etc., are constants which we have to find. From these expressions we deduce for the effective cross-sections Q_0, Q_n for elastic and inelastic collisions respectively,

$$Q_0 = \frac{\pi}{k^2} \sum_s (2s+1)\{4|q_0^s|^2 + 4\sin^2\eta_0^s - 4q_0^s \sin\eta_0^s \cos\eta_0^s\},$$

$$Q_n = \frac{\pi}{kk_n} \sum_s (2s+1)|q_n^s|^2. \tag{26}$$

When $|q_n^s|^2$ is small compared with unity, it may be calculated readily

† Cf. Chap. VIII, Fig. 11.

by Born's approximation;† we obtain

$$q_n^s = \frac{4\pi^3 M}{h^2} \int_0^\infty V_{0n} J_{s+\frac{1}{2}}(kr) J_{s+\frac{1}{2}}(k_n r) r \, dr. \tag{27}$$

No matter how large V_{0n} may be, this formula will hold for sufficiently large s; but for such s that the formula (27) gives $q_n^s > \frac{1}{2}$, it is completely incorrect, and other methods must be used.

A method similar to that of Chap. VII, § 3, has been given by Stueckelberg (loc. cit.) for the case V_{0n} large. Stueckelberg expands F_0^s in the form
$$F_0^s = r^{-1} \exp\{h^{-1}(S_0 + hS_1 + h^2 S_2 + \ldots)\}, \tag{28}$$
and solves the equation for F_0^s obtained by eliminating F_n^s from the equations (16), and neglecting terms of order higher than h. The form of the solution depends on whether the function

$$k^2 - k_n^2 - 8\pi^2 M(V_{00} - V_{nn})/h^2 \tag{29}$$

has a real positive zero. If such a zero R exists, Stueckelberg obtains the following formulae for q, η. In these formulae the index s is omitted.

If we write

$$(\mu_n)^2 = k_n^2 - U_{nn} - s(s+1)/r^2, \qquad U_{nn} = 8\pi^2 M V_{nn}/h^2$$

with a similar expression for μ_0, and further

$$A = \tfrac{1}{2}(k^2 + k_n^2 - U_{00} - U_{nn}) - s(s+1)/r^2,$$
$$B = \tfrac{1}{2}[(k^2 - k_n^2 - U_{00} + U_{nn})^2 + 4(U_{0n})^2]^{\frac{1}{2}},$$
$$(\nu_0)^2 = A + B, \qquad (\nu_n)^2 = A - B,$$
$$N_n = \int_R^R \nu_n \, dr, \qquad M_n = \int^\infty \mu_n \, dr,$$

where the lower limit of integration is the zero of the integrand, and further

$$\beta = N_n - M_0 + \int_R^\infty \nu_0 \, dr, \qquad \gamma = -N_0 + M_n - \int_R^\infty \nu_n \, dr, \qquad \tau = N_n - N_0,$$

then

$$q_0 = -i e^{-i\beta}[e^{-i(\tau+\beta)}(1 - e^{-2\delta})\sin \tau + \sin \beta],$$
$$q_n = -i e^{i(\beta-\gamma)} e^{-\delta}(1 - e^{-2\delta})^{\frac{1}{2}} \sin \tau,$$
$$\eta_0 = 2N_n + 2 \int_R \nu_0 \, dr - M_0 - \tfrac{1}{4}(2s+1)\pi \tag{30}$$

The quantity δ (i.e. δ_s) which occurs in these formulae, and which is of

† Loc. cit.

primary importance in determining the magnitude of the cross-section, is equal to the value, at $r = R$, of

$$\pi(U_{0n})^2 \Big/ 2\left\{\frac{d}{dr}(U_{00}+U_{nn})\right\}(v_0+v_n).$$

To calculate the cross-section Q_n with fair approximation when Born's formula is not valid for all s, it is necessary to calculate q_n^s from (30) for small values of s, and from (27) for large values, interpolation being used to obtain values for the few intermediate values of s. This method has not been applied in detail to any particular case, since the potentials V_{00}, V_{nn}, and V_{0n} for atomic collisions are not known with sufficient accuracy to warrant such detailed calculation. It is quite clear, however, that this method predicts a smaller probability than does Born's approximation; Stueckelberg has shown that, when the zero R exists, the maximum possible value of Q is roughly πR^2.

The theory discussed above predicts the existence of resonance phenomena, similar to those predicted by the more approximate theory of § 3.31; it shows also that the cross-section in the neighbourhood of the resonance point may attain a much greater value when there is no 'crossing point' R than when such a point exists. In fact, the cross-section in the former case may be very much greater than the gas-kinetic cross-section. Typical resonance curves for the two cases are illustrated in Fig. 50.

In both cases the relative velocity of the systems corresponds to one electron volt and M is 10 times the mass of a hydrogen atom.

It may also be pointed out that the method of solving the coupled equations (16) outlined above may be applied to inelastic collisions of electrons with atoms; for this case V_{00}, V_{nn}, and V_{0n} are well known.

3.4. *Passage of Positive Ions through Gases.*

In this section we consider the collisions of positive ions of energy greater than, say, 50 volts with gas atoms. The types of collision which occur may be classified as follows:

1. Elastic collisions.
2. Collisions resulting in the neutralization of the ion by electron capture from the gas atoms.
3. Inelastic collisions resulting in excitation or ionization either of the gas atoms or the incident ions.

The cross-section for elastic collisions must be calculated by the Method of Partial Cross-sections (Chap. II, § 1) and is given in terms

of the phase constants by the series

$$Q = \frac{4\pi}{k^2} \sum (2n+1)\sin^2\eta_n. \tag{31}$$

k is, as usual, equal to $2\pi/$wave-length. A large number of terms of this series are required (at least 400 for 100-volt protons in helium);
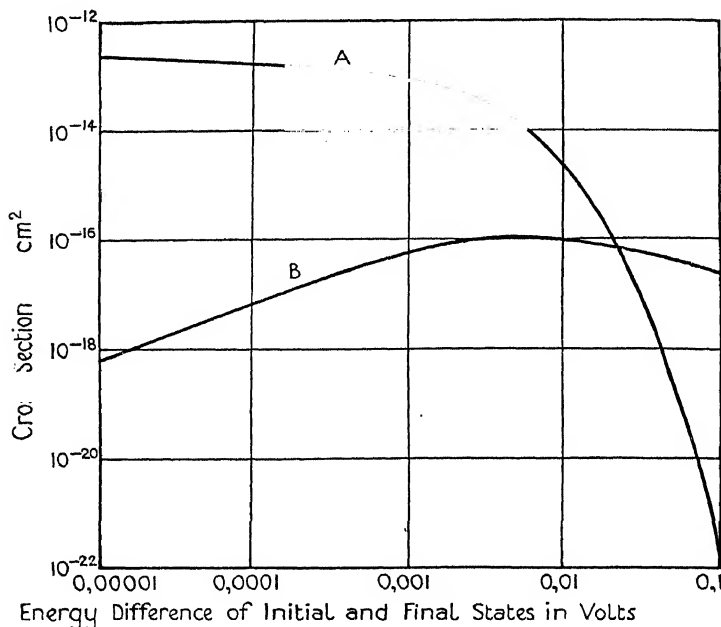
FIG. 50. Calculated cross-sections for collisions of the second kind between atoms, as a function of the 'Resonanz-Unschärfe'.
  A. Calculated with no crossing point, for $V_{0n} = c/r^3$.
  B. Calculated assuming a crossing point, for $V_{0n} = c/r^2$.

but the summation over a certain range of n may be replaced by an integral. Use may also be made of the oscillatory nature of $\sin\eta_n$ when n is small (less than 200 for 100-volt protons in helium). Some calculated values of Q for the collisions of protons with helium and argon are given in Table II.

It will be seen that these calculated cross-sections do not differ greatly from the gas-kinetic values; yet experimental determinations† of the

† Dempster, *Phil. Mag.*, 3 (1927), 115; Ramsauer, Kollath, and Lilienthal, *Ann. der Phys.*, 8 (1931), 709.

TABLE II

Gas.	Proton Energy in e. volts.	Cross-section in units of πa_0^2.	Gas Kinetic Cross-section in units of πa_0^2 (exptl.).
He	90	3·7	2·6
	800	2·0	
A	73	16·4	7·3
	650	10·7	

free paths of protons in both helium and argon have indicated much smaller total cross-sections than the gas-kinetic. However, the reason for this is clear when the angular distribution of the scattered protons is considered. This may be calculated by classical methods† except at very small angles of scattering, and it may be shown that the limiting value of the angular distribution function $I(\theta)$ for zero angle of scattering is approximately $\frac{1}{4}k^2Q^2$ which is $\gg Q$ except for very slow ions ($< \frac{1}{10}$ volt). Combining these results it is found that the scattered intensity falls off so rapidly with increasing angle of scattering that only a small fraction of the elastic collisions occurring could be observed in the experiments cited.

Collisions in which an electron is captured by the ion are usually inelastic, as the mutual kinetic energy is altered by the collision. In the special case of exact resonance which occurs, for example, when a helium positive ion captures an electron from a helium atom, the collisions are elastic in the sense that the mutual kinetic energy remains unaltered. It is not strictly correct to assign a cross-section for charge transfer in the case of exact resonance, as it is impossible to determine experimentally whether an ion observed in any given direction is the incident ion which has been scattered or a struck atom which has lost an electron. Actually the observations show that large numbers of positive ions are produced moving in directions nearly perpendicular to the incident beam. As we know from experiments in which the incident ions are distinguishable from atoms which have lost an electron, that very few ions are directly scattered in such directions, we may arbitrarily consider that all ions which move in directions making angles greater than, say, 45° with the direction of incidence, are struck atoms which have lost one electron, all the remaining ions arising by direct scattering from the incident beam. Since the observed absorption of, say, He$^+$ ions in He is mainly due to large angle deviations, we may say, on the basis of our assumption, that the absorption is mainly due

† Cf. Chap. VII, § 3, for the proof of this statement.

to charge transfer. To calculate the absorption cross-section we may then use the formula given in Chap. VIII, § 3.2, for the limiting value of the probability of an inelastic collision in the case of exact resonance. This calculation follows on the same lines as that of the elastic cross-section given earlier in this section, and it is found that the absorbing cross-section due to transfer of charge is comparable with the gas-kinetic cross-section, in agreement with the experiments of Kallmann and B. Rosen.† A more exact theory, which takes account of the identity of the nuclei (cf. Chapter V) will only modify the form of the angular distribution of the scattered ions at intermediate angles of scattering, where maxima and minima will occur due to the interference of the two types of scattered waves. Since the contribution to the cross-section arising from these angles is very small, this effect is unimportant, except for precise measurements of angular distributions.

When electron capture requires change of kinetic energy, the theory of the process must follow on exactly similar lines to that of excitation and ionization by the ions. Since the velocity of the ions is small compared with the orbital velocities of the atomic electrons, and since there are few cases where the resonance between initial and final states is so close as to permit of the consideration of the interaction of these two states alone, the only method which is satisfactory for the discussion of these processes is the Method of Perturbed Stationary State Wave Functions discussed in Chap. VIII, § 3.3.

This method has been applied‡ to the calculation of the cross-sections for excitation of the $2\,^1P$ state of helium by protons, and for electron capture by protons. The excitation cross-section is illustrated as a function of the energy of the protons in Fig. 48. Similar curves are obtained for the capture cross-section. For purposes of contrast the corresponding curve for electrons is also shown in the figure. The obvious difference in the calculated behaviour of the two particles is shown also by the experimental results, both for excitation and ionization.§

A further important result of the calculations is that the probability of the collision is negligible until the energy of the incident proton exceeds a certain value, which is considerably greater than the excitation energy. This 'activation energy' can be shown in general to be approximately proportional to‡

$$M(\Delta E)^2 R_0^2, \tag{32}$$

† *Zeits. f. Physik*, **64** (1930), 808.
‡ Massey and Smith, *Proc. Roy. Soc.*, A, in course of publication.
§ *Vide* Döpel, *Ann. der Phys.*, **16** (1933), 1.

where ΔE is the excitation energy, M the reduced mass of the colliding systems, and R_0 is the sum of their radii. The existence of this activation energy, which is not predicted by Born's approximation (see Fig. 51), is confirmed by the experimental results; and the available evidence also indicates that it is of the order of magnitude given by
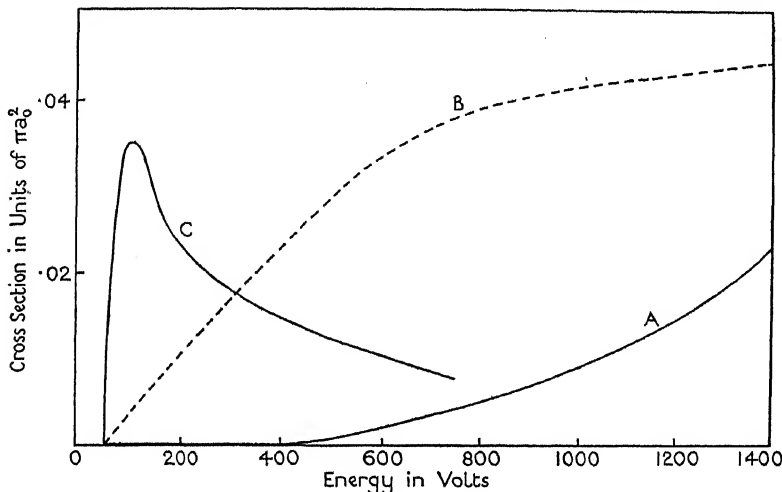
FIG. 51. Cross-sections for excitation of the 2^1P level of helium.
A. Calculated for protons using Method of Perturbed Stationary States.
B. Calculated for protons using Born's approximation.
C. Calculated for electrons. (This curve has been drawn on one-third the scale to facilitate comparison.)

(32). Thus Appleyard† showed that sodium ions with energy between 300 and 3,000 volts can excite mercury atoms ($\Delta E = 5$ volts), but are not appreciably excited themselves (requiring $\Delta E = 32$ volts). Again Döpel‡ has found that hydrogen atoms with less than 1,000 volts energy can excite potassium and sodium atoms ($\Delta E = 2$ volts) quite strongly, although even when their energy is increased to 20,000 volts there is no indication that they are ever excited themselves by the collision (requiring $\Delta E = 10$ volts).

The study of the passage of positive ions through gases is by no means in a final stage, either from an experimental or theoretical point of view. References to further work are given below.§

† *Proc. Roy. Soc.*, A, **128** (1930), 330.   ‡ *Ann. der Phys.*, **16** (1933), 1.

§ For experimental material see J. J. and G. P. Thomson's *Conduction of Electricity through Gases*, Part II, Chap. IV, 1933. For theoretical work see Massey and Smith (loc. cit.), where further references to this branch of the subject are given.

3.5. *Exchange of Energy between Translational Motion and Molecular Vibration and Rotation.*

In this section we shall discuss methods by which one may calculate the probability that a molecule will change its vibrational or rotational state under impact from another atom. For this purpose we require to know the interaction energy between the molecule and atom.

The theoretical treatments given at present have been confined to impacts in which the striking atom moves along the line joining the nuclei of a diatomic molecule; the vibrational transition probabilities will probably be greatest for such impacts. We need, then, only consider the interaction of the striking atom with one of the atoms of the molecule (of mass M_B, say). A form of the interaction energy which probably gives a very good approximation near the distance of closest approach is

$$Ce^{-ar}, \tag{33}$$

where r is distance between the atom M_B and the striking atom. The constant a may be determined by comparing (33) with the potentials deduced by Lennard-Jones† from experimental measurements of the viscosity and thermal conductivity of gases.

If we denote by R the distance between the nuclei of the striking atom and the centre of gravity of the molecule, and by ρ the distance between the vibrating nuclei of the molecule, then (33) may be written

$$V(R,\rho) = e^{-a(R+\lambda\rho)}, \tag{34}$$

where $$\lambda = M_C/(M_B+M_C),$$

and M_C is the mass of the other nucleus in the molecule. If we assume that the vibration is simple harmonic, the vibrational wave functions are Hermite polynomials. Owing to the fact that the amplitude of the nuclear vibration is small compared with the length $1/a$, the non-diagonal matrix elements of V with respect to the vibrational wave functions are small. The method of Chap. VIII, § 3.3 (perturbation method with distorted waves), may thus be used to calculate the transition probabilities with considerable accuracy.

Such calculations have been carried out by Zener‡ using a simplified field, and by Jackson and Mott§ using the field (34). With the latter field the following results are obtained for a head-on collision such as that described. We denote by $p_{n,m}$ the probability per collision that the vibrational quantum number changes from n to m; M_A is the mass

† R. H. Fowler, *Statistical Mechanics*, Chap. X, 1929.
‡ *Phys. Rev.*, 37 (1931), 556.

§ Cf. § 3.6.

of the striking atom, v_n the relative velocity before the collision, v_m afterwards. Then

$$p_{n,m} = \frac{32\pi^4}{h} \frac{M_C(M_B+M_C)M_A^2}{a^2 M_B(M_A+M_B+M_C)^2}(n+\tfrac{1}{2}\pm\tfrac{1}{2})\nu \times$$

$$\times \frac{\sinh \pi q_n \sinh \pi q_m}{(\cosh \pi q_n - \cosh \pi q_m)^2}, \qquad m = n\pm 1,$$

where

$$q_n = 4\pi M^* v_n/ha,$$
$$q_m = 4\pi M^* v_m/ha,$$
$$M^* = M_A(M_B+M_C)/(M_A+M_B+M_C),$$

and ν is the natural frequency of the vibrator. The probability of an energy change in which n changes by more than 1 is very small, except for high energies of impact.

The chief interest of this formula is that it shows that exchange of energy between translation and vibration takes place only with difficulty. Thus in the one-dimensional collisions of helium with nitrogen at room temperature, the probability of deactivation of the molecule from the first vibrational state is of the order 6×10^{-7}. It is the very low probability of exchange of vibrational and translational energy which accounts for the failure of the velocity of sound method of determining the specific heats of gases, at high temperatures.[†]

Similar methods may be applied to the consideration of the transfer of excitation of vibration between two molecules on impact. It is found then that, even in the case of exact resonance, the probability of transfer of vibrational energy may be very small. The resonance cross-section increases with the reduced mass of the two molecules and the kinetic energy of relative motion, while the resonance effect is sharpest for heavy molecules.

Rice[‡] has applied the theory to the consideration of the activation of various complex molecules by impact with similar molecules, with inert gas atoms, and with hydrogen. He finds that hydrogen is as efficient in activation as these molecules, and is much more so than the inert gases. This is in general agreement with the chemical evidence.

The theory of the excitation of rotational motion is less well developed, but it appears that transfer of energy between translation and rotation can take place relatively easily.[§] The probability of such a transfer will naturally depend very largely on the symmetry of the molecule. In particular, if the molecule is excited to such a high

† Cf. § 1.5 of this chapter.   ‡ *Chemical Reviews*, **10** (1932), 125.
§ Zener, *Phys. Rev.*, **37** (1931), 556.

electronic state that the charge distribution is nearly spherically symmetrical, the excitation of rotation will be difficult. This is in agreement with observation.†

3.6. *The Collisions of Atoms with Crystals.*

3.61. *Accommodation Coefficients.* The recent experiments of Stern and Estermann‡ have shown that molecules may be elastically reflected by crystal surfaces, and that cross-grating diffraction effects may be obtained, due to the interference of the de Broglie waves of the molecules. The intensity of the diffracted beams shows that a large fraction of the molecules are reflected without energy interchange with the crystal; the measurements of thermal accommodation coefficients confirm this result.

The thermal accommodation coefficient α of a solid surface for gas atoms at temperature T is defined as

$$\alpha(T) = \lim_{T_g \to T_s \to T} \frac{T'_g - T_g}{T_s - T_g},$$

where T_g is the temperature of the gas atoms before striking the solid at temperature T_s, and T'_g is their temperature after a single collision. It is obvious that α is a measure of the probability of energy exchange between the gas atoms and the vibrational motion of the solid lattice. The low value of α is then due to the small probability of these exchanges. The theory of § 3.5 is at once applicable and has been applied to the problem by Jackson and Mott.§ One-dimensional collisions are considered and the formula (37) for the transition probability used. Comparison of the resulting expressions for $\alpha(T)$ with the experiments of Roberts,‖ carried out with helium gas and tungsten surfaces, reveals very good agreement. Taking an exponential field Ce^{-ar} between the gas atom and solid surface, and a value of a of about 8×10^8 cm.$^{-1}$, the calculated variation of α with temperature agrees well with the observed. It is difficult to compare the absolute magnitudes of α with theory, owing to the microscopic roughness of the tungsten wire, which makes the effective area open to collisions uncertain. Nevertheless, the success of the theory shows that the study of accommodation coefficients will lead to valuable information about the interaction of atoms.

For gases other than helium the large van der Waals attractive forces must be taken into account; at the time of writing this has not been done in a satisfactory way.

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† Rompe, *Zeits. f. Physik,* **65** (1930), 428.
‡ *Zeits. f. Physik,* **61** (1930), 95. § *Proc. Roy. Soc.,* A, **137** (1932), 703.
‖ *Proc. Roy. Soc.,* A, **129** (1930), 146, and **135** (1932), 192.

3.62. *Electron Emission from Metals due to Impact of Positive Ions and Metastable Atoms.* It has long been known that positive ions are capable of ejecting electrons from metal surfaces† when not in thermal contact with the surface; Oliphant‡ and others have shown that metastable atoms of helium are capable of producing similar effects.

The general explanation of the phenomena has been discussed by Oliphant and Moon,§ who show that the effects are due to collisions of the second kind with the metal electrons, in which the atom is deactivated and a metal electron receives sufficient energy to carry it over the surface potential barrier of the metal. The probability of such collisions is quite high, as has been shown by a quantum-mechanical treatment in which the atom is considered as a slowly moving point and the metal electrons considered as colliding with the atom.‖ The cross-section for a collision of the second kind may then be computed. For further detail we refer the reader to the original papers.

† *Vide* Oliphant, *Proc. Roy. Soc.*, A, **127** (1930), 373.
‡ Ibid. **124** (1929), 228.
§ Ibid. **127** (1930), 388.
‖ Massey, *Proc. Camb. Phil. Soc.*, **26** (1930), 386, and **27** (1931), 460.

XIV

TRANSITION PROBABILITIES BY METHOD OF VARIATION OF PARAMETERS

1. Introduction

The problems of quantum mechanics may conveniently be divided into two classes: the calculation of the eigenvalues of the energy and of the other observables of a dynamical system; and the calculation of the probability that a system will make a transition from one state to another under a given perturbation. Our aim in this chapter is to summarize the methods available for the solution of the latter class of problem. The previous chapters have been mainly concerned with the calculation of a particular type of transition probability, namely, that between two states of equal unquantized energy, due to a perturbation (interaction between atom and colliding particle) which is *not* a function of the time. For this type of problem we have found it convenient to use a periodic wave function, containing the time in the exponential factor $\exp(-2\pi i Wt/h)$ only. In this chapter we consider methods for the calculation of transition probabilities between states one of which is quantized; for such problems a periodic wave function cannot be used, and the 'Method of Variation of Parameters' must be employed.†

The transition probabilities calculated in this chapter may be divided into two classes in the following way:

I. Transitions, due to a perturbing field which is not a function of the time, from a quantized state to an unquantized state of equal energy. Examples of this kind of problem are: Gamow's theory of radioactive decay;‡ the Auger effect;§ the spontaneous dissociation of a molecule in a high rotational state. Perturbation theory is particularly suitable for the solution of this kind of problem, because, if the perturbing field is not 'small', it is impossible to use the conception of a transition probability. This may be seen most easily by reference to the Auger effect, where one has to calculate the probability that if two electrons are in excited states in one atom, one of them will fall to the ground state, giving up its energy to the other electron, which is thereby ejected from the atom. The 'perturbing energy' is here the interaction potential energy of the two electrons; if this is not 'small', so that the

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† The method was first given by Dirac, *Proc. Roy. Soc.*, A, **114** (1929), 243.
‡ *Atomic Nuclei and Radioactivity*, Oxford, 1931, p. 30.
§ Auger, *J. Phys. Rad.*, **6** (1925), 205.

probability is small of the transition taking place in a time equal to the period of the atom, then it is meaningless to speak of the electrons as being initially in definite stationary states.

This is *not* true of transitions between two unquantized states. For such problems the validity of the perturbation method depends on the quite different considerations discussed in Chap. VII, § 2, and elsewhere in this book.

II. Transitions due to a perturbing field which is a function of the time. Here the initial and final states may be of different energy. Both the initial and final states may be quantized or unquantized. Examples are: the excitation and ionization of an atom by collision with an α-particle, when the α-particle is treated as a moving centre of force; the absorption of radiation and the photoelectric effect, when the light wave is not treated as a quantized field.

Transitions under the heading I may be considered as a special case of II. We shall therefore consider transition probabilities in the following order:

Transitions caused by a perturbing function which is a function of the time:

(a) Final state quantized.

(b) Final state in range of continuous energies.

Transitions caused by a perturbing function which is a periodic function of the time.

Transitions caused by a perturbation independent of the time.

2. Excitation of an Atom by a Perturbation which is a Function of the Time

For simplicity we take for the unperturbed system a single electron moving in the field of an infinitely heavy nucleus. Let $\mathbf{r}$ denote the coordinates of the electron, H the Hamiltonian of the unperturbed atom, and $\psi_s(\mathbf{r})$, W_s the wave functions (not functions of t) and energy values of the stationary states, satisfying the equation

$$(H - W_s)\psi_s = 0. \tag{1}$$

We suppose the system to be perturbed by an energy term $V(\mathbf{r}, t)$, and the atom to be initially ($t = t_0$) in the state $s = 0$, the wave function being therefore initially

$$\psi_0(\mathbf{r})\exp(-2\pi i W_0 t/h). \tag{2}$$

At any subsequent time let the wave function be $\Psi(\mathbf{r}, t)$; then Ψ may

be determined from the initial condition (2) and from the wave equation

$$-\frac{h}{2\pi i}\frac{\partial \Psi}{\partial t} - H\Psi = V\Psi. \tag{3}$$

To interpret Ψ we expand it in the form

$$\Psi(\mathbf{r}, t) = \sum_s a_s(t)\psi_s(\mathbf{r})\exp(-2\pi i W_s t/h), \tag{4}$$

and make the assumption that $|a_s(t)|^2$ is equal to the probability that the atom is in the state s at time t (for quantized states; for unquantized states cf. § 2.1). We have therefore to calculate the coefficients $a_s(t)$. Substituting (4) in the *left*-hand side of (3), we obtain

$$-\frac{h}{2\pi i}\sum_s \left[\frac{d}{dt}a_s(t)\right]\psi_s(\mathbf{r})\exp(-2\pi i W_s t/h),$$

which is therefore equal to $V\Psi$. Hence, if we multiply both sides of this equation by any one of the functions $\psi_s^*(\mathbf{r})\exp(+2\pi i W_s t/h)$ and integrate over all $\mathbf{r}$, we obtain

$$\frac{d}{dt}a_s(t) = -\frac{2\pi i}{h}\exp(2\pi i W_s t/h)\int \psi_s^*(\mathbf{r})V(\mathbf{r}, t)\Psi(\mathbf{r}, t)\,d\mathbf{r}. \tag{5}$$

Initially, at time $t = t_0$, all the a_s are zero, except for a_0, which is equal to unity; hence, integrating (5), we obtain, if $s \neq 0$,

$$a_s(t) = -\frac{2\pi i}{h}\int_{t_0}^{t} dt\left\{\exp(2\pi i W_s t/h)\int \psi_s^*(\mathbf{r})V(\mathbf{r}, t)\Psi(\mathbf{r}, t)\,d\mathbf{r}\right\}. \tag{6}$$

This equation is exact. It cannot, however, be used to evaluate a_s, since the right-hand side contains the unknown function Ψ. If, however, it is permissible to assume that during the perturbation $\Psi(\mathbf{r}, t)$ is only slightly different from its original form, we may replace Ψ by $\psi_0(\mathbf{r})\exp(-2\pi i W_0 t/h)$ in the right-hand side of (6), and write

$$a_s(t) = -\frac{2\pi i}{h}\int_{t_0}^{t} V_{s0}(t)\exp\{2\pi i(W_s - W_0)t/h\}\,dt, \tag{7}$$

where

$$V_{s0}(t) = \int \psi_s^*(\mathbf{r})V(\mathbf{r}, t)\psi_0(\mathbf{r})\,d\mathbf{r}. \tag{8}$$

It is permissible to make this approximation if the perturbing energy is 'small'. The significance of this statement depends on the type of perturbation under consideration. We consider first the perturbation due to a heavy charged particle of charge E passing the atom, the particle being treated as a moving centre of force.

If the nucleus of the atom is at the origin, and the position of the perturbing particle at time t is

$$\mathbf{R} = (X, Y, vt),$$

then

$$V(\mathbf{r}, t) = -\epsilon E/|\mathbf{R} - \mathbf{r}|. \tag{9}$$

The probability that the atom will be left in the state s after the collision is $|a_s(\infty)|^2$, where

$$a_s(\infty) = -\frac{2\pi i}{h} \int\limits_{-\infty}^{+\infty} V_{s0}(t) \exp[2\pi i(W_s - W_0)t/h] \, dt. \tag{10}$$

The perturbation method is valid here if the wave function is only slightly perturbed during the collision. This is obviously true for distant collisions, and may be shown to be true for collisions in which the particle passes through the atom, if its velocity is so great that the time during which the perturbation is effective is small. The method is also valid if the charge E on the particle is small compared with $Z\epsilon$. A *necessary* condition for the validity of the approximate method is

$$\sum_s |a_s(\infty)|^2 \ll 1.$$

The condition is not sufficient; for instance, for very slowly varying perturbations, $a_s(t)$ may be comparable with unity *during* the collision, even though $a_s(\infty)$ is small.†

If the perturbation is due to a light wave, we require to find the probability, $P_s \Delta t$, that the atom is excited to the state s in time Δt. Writing $\sum P_s = P$, the probability after time t that the atom remains in its normal state is then e^{-Pt}, it being of course assumed that spontaneous emission of radiation does not take place. The perturbation method will thus be valid for t such that

$$Pt = \sum_s |a_s(t)|^2 \ll 1.$$

Such perturbations are considered further in § 3, and it is shown that the method always gives an accurate value of P_s, unless the light wave is of intensity great enough to excite the atom in a time comparable with $1/\nu$, which is in practice never the case.

2.1. *Ionization of an Atom by a Perturbation which is a Function of the Time.*

The wave function $\Psi(\mathbf{r}, t)$ describing the atom after the perturbation must contain terms which describe ionized states of the atom. The

† Cf. Chap. VIII, § 3.2.

expansion (3) is thus not complete; we must replace it by

$$\Psi(\mathbf{r}, t) = \sum a_s \psi_s \exp(-2\pi i W_s t/h) + \int a_W(t) \psi_W(\mathbf{r}) \exp(-2\pi i W t/h)\, dW,$$

$$(11)$$

where the functions $\psi_W(\mathbf{r})$ are the solutions of (1) for positive energy. These solutions are of the form

$$\psi_W(\mathbf{r}) = S_n^u(\theta, \phi) N L_{nW}(r),$$

where S_n^u is the normalized spherical harmonic given by

$$S_n^u = [(2n+1)(n-u)!/4\pi(n+u)!]^{\frac{1}{2}} P_n^u(\cos\theta) e^{iu\phi},$$

and L is the radial part of the wave function normalized so that† [Chap. II, eq. (15)]

$$L \sim (kr)^{-1} \sin(kr - \tfrac{1}{2}n\pi + \eta_n)$$

and N is a constant. In (11) a summation over all values of n, u is to to be understood. If we set

$$N = N(W) = 2k(hv)^{-\frac{1}{2}},$$

$$(12)$$

then it may be shown‡ that the function G defined by

$$\int^R \psi_{Wnu}(\mathbf{r}) \psi_{W'nu}(\mathbf{r})\, d\tau = G(W, R),$$

where the integration is over a sphere of radius R, has the following property: if $f(W)$ is any function of W, then

$$\lim_{R \to \infty} \int_0^\infty G(W, R) f(W)\, dW = f(W').$$

This property of the function $G(W, R)$ is conveniently expressed by the statement

$$G(W, \infty) = \delta(W - W'),$$

where δ is the 'δ-function' of Dirac.§

Making use of (12), it is easy to show that

$$a_W(t) = -\frac{2\pi i}{h} \int_{t_0}^t V_{W0}(t) \exp[2\pi i(W - W_0) t/h]\, dt.$$

$$(13)$$

The wave function may be deduced from (11).

We shall now deduce from the wave function (11) the probability that the electron is ejected from the atom. We shall suppose that the perturbing function is operative only from time $t = 0$ to time $t = T$. We shall calculate the probability, $P\, dv_0\, d\omega$, that, during this time interval, the electron is ejected in a direction lying in a solid angle $d\omega$

† The term $(2\pi Z\epsilon^2/hv)\log 2kr$ which occurs for Coulomb fields is omitted.
‡ Sommerfeld, *Wave Mechanics*, p. 290.   § *Quantum Mechanics*, p. 63.

about the direction given by the unit vector $\mathbf{n}$, and with velocity lying between v_0, $v_0 + dv_0$.

For this purpose we investigate the asymptotic form of $\Psi'(\mathbf{r}, t)$ for values of $\mathbf{r}, t$ given by $\mathbf{r} = \mathbf{n} v_0 t$ for values of the time t so long after the perturbation has ceased that

$$t\, dv_0 \gg T v_0.$$

Under these conditions it is clear that

$$
\begin{aligned}
P\, dv_0\, d\omega &= |\Psi|^2 r^2\, dr\, d\omega \\
&= |\Psi|^2 t^3 v_0^2\, dv_0\, d\omega.
\end{aligned}
\tag{14}
$$

The right-hand side must be independent of t, and we shall show that this is the case.

We have then to investigate (11) for large r, t. The coefficient $a_W(t)$ given by (13) tends to a constant value as $t \to \infty$, since the perturbing energy V is assumed to be finite only in the time interval $0 < t < T$. Replacing $\psi_W(\mathbf{r})$ by its form for large r, we see that the only terms in the integral in (11) which involve r, t are

$$(kr)^{-1} \sin(kr - \tfrac{1}{2}n\pi + \eta_n) e^{-2\pi i W t / h},$$

which may be written

$$
(2ikr)^{-1} \Big\{ \exp\Big[\frac{2\pi i m}{h}(vr - \tfrac{1}{2}v^2 t) - \tfrac{1}{2}n\pi i + i\eta_n\Big] - \\
- \exp\Big[\frac{2\pi i m}{h}(-vr - \tfrac{1}{2}v^2 t) + \tfrac{1}{2}n\pi i - i\eta_n\Big] \Big\}.
\tag{15}
$$

The range of integration in (11) is from $W = 0$ to $W = \infty$, and hence from $v = 0$ to $v = \infty$. The first of the two terms in (15) has a stationary point† in this range, for $v = r/t$, and, for r, t sufficiently large, the whole integral comes from the neighbourhood of this point.† The second term in (15), which corresponds to an *ingoing* wave, has no such point in the range, and therefore makes a contribution to the integral of higher order in $1/t$. It may therefore be neglected.

The first term in (15) may be written

$$(2ikr)^{-1} \exp\Big[\frac{2\pi i m}{h}\{-\tfrac{1}{2}t(v - v_0)^2 + (v_0 r - \tfrac{1}{2}v_0^2 t) - \tfrac{1}{2}n\pi i + i\eta_n\}\Big],
\tag{16}$$

where $v_0 = r/t$. Making use of the formula

$$\int_{-\infty}^{+\infty} \exp(iA\zeta^2)\, d\zeta = (\pi/iA)^{\frac{1}{2}} \qquad (\zeta = v - v_0, \quad A = -\pi m t / h),$$

† i.e. the function $e^{iU(v)}$ is said to have a stationary point for any value of v for which $f'(v) = 0$. The theorem quoted may easily be proved by deforming the path of integration into the complex plane.

we obtain from (11), putting $dW = mv\,dv$,

$$|\Psi| \sim \Big|\sum_{n,u} a_{W_0\,nu}(\infty)N(W_0)(2ik_0 r)^{-1}(h/mt)^{\frac{1}{2}}mv_0\exp(-\tfrac{1}{2}n\pi i+i\eta_n)S_n^u(\theta,\phi)\Big|,$$

where $$W_0 = \tfrac{1}{2}mv_0^2, \text{ etc.}$$

This may be written

$$|\Psi| \sim r^{-1}(mv_0/t)^{\frac{1}{2}}|f(\theta,\phi)|, \tag{17}$$

where $\quad f(\theta,\phi) = (h/v_0)^{\frac{1}{2}}\sum_n\sum_u \exp(i\eta_n-\tfrac{1}{2}n\pi i)S_n^u(\theta,\phi)a_{W_0\,nu}(\infty),$

and where $r = v_0 t$. It will be seen that $|\Psi|^2$ is proportional to t^{-3}. From (14) we deduce that

$$P\,dv_0\,d\omega = (mv_0^2/h)|f(\theta,\phi)|^2\,dv_0\,d\omega. \tag{18}$$

Further, integrating over all θ,ϕ, we find that the total probability that a particle is ejected with energy between W, $W+dW$ is

$$\sum_n\sum_u|a_{Wnu}(\infty)|^2\,dW. \tag{19}$$

An alternative form may be given for $f(\theta,\phi)$. Inserting the formula (13) for a_W in (16) and referring to formulae Chap. II, (16), and Chap. VI, (24), we obtain

$f(\theta,\phi)$

$$\frac{2\pi m}{h^2}\int d\tau'\int_{-\infty}^{+\infty}dt\,\mathfrak{F}(r',\pi-\Theta)V(\mathbf{r'},t)\psi_0(\mathbf{r'})\exp[2\pi i(W-W_0)t/h]. \tag{20}$$

Here $\quad\cos\Theta = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi-\phi'), \tag{21}$

and $\mathfrak{F}(r,\theta)$ is the function discussed in Chap. II, § 1—i.e.

$$\mathfrak{F}(r,\theta) = \sum_n (2n+1)i^n e^{i\eta_n}P_n(\cos\theta)L_n(r),$$

which has asymptotic form

$$\mathfrak{F} \sim e^{ikz}+r^{-1}e^{ikr} \times \text{function of }\theta.$$

The function $\mathfrak{F}(r',\pi-\Theta)$ thus represents a plane wave in the opposite direction to θ,ϕ together with an *outgoing* wave, and is thus *not* the complex conjugate of the wave function of the final state. It is only when the influence of the nucleus on $\mathfrak{F}$ may be neglected (fast electrons, small atomic number, $2\pi Ze^2/hv \ll 1$), so that $\mathfrak{F}(r',\pi-\Theta)$ may be replaced by $\exp(-ik\mathbf{n\cdot r'})$, that $\mathfrak{F}$ may be considered as the complex conjugate of the final state.†

3. Transitions due to a Perturbing Function Periodic in the Time.

We take for the perturbing potential

$$V(\mathbf{r},t) = \lambda U(\mathbf{r})e^{-2\pi i\nu t}+\lambda U^*(\mathbf{r})e^{2\pi i\nu t}, \tag{22}$$

where U is a function of r but not of t, and λ is a parameter. Assuming

† Cf. Chap. III, p. 36, note at end of § 2.

that the perturbed system is in the state 0 at time $t = 0$, then at time t the wave function is, from (13),

$$\sum_s a_s(t)\psi_s(\mathbf{r})\exp(-2\pi i W_s t/h)+$$
$$+ \int a_W(t)\psi_W(\mathbf{r})\exp(-2\pi i W t/h)\, dW, \qquad (23)$$

where

$$a_s = \frac{\exp[2\pi i(W_s - W_0 - h\nu)t/h] - 1}{W_s - W_0 - h\nu}\lambda U_{s0} +$$
$$+ \frac{\exp[2\pi i(W_s - W_0 + h\nu)t/h] - 1}{W_s - W_0 + h\nu}\lambda U_{s0}^*, \qquad (24)$$

and

$$U_{s0} = \int \psi_s^*(\mathbf{r})U(\mathbf{r})\psi_0(\mathbf{r})\, d\tau, \qquad (25)$$

with a similar expression for a_W.

In order to obtain results of physical significance in problems where V is periodic, one must take t, the time during which the perturbation acts, to be great in comparison with $1/\nu$. One requires the probability $P_s \Delta t$ per time Δt ($\Delta t \gg 1/\nu$) that the atom will be excited or ionized, in contradistinction to the problem considered in § 2.1, where the probability of excitation during a single event (collision) was required. Denoting by $P = \sum P_s$ the total probability per unit time of excitation or ionization, then the probability that after time t the atom is still in its normal state is e^{-Pt}. The perturbation method used (cf. § 2.1) to obtain (25) is only correct for values of t such that this probability is not very different from unity, i.e. if

$$Pt \ll 1. \qquad (26)$$

However, if the perturbation is due to a light wave, P_s will be proportional to its intensity, i.e. to λ^2, and in calculating P_s we may take λ as small as we please. Thus it is always possible to choose t so that (26) shall be satisfied, consistently with the inequality $t \gg 1/\nu$. The perturbation method thus gives accurate results for intensities of perturbing field such that P is proportional to λ^2, which is the case for all light waves.

The method of interpretation depends on whether the final state is quantized or whether it lies in the range of continuous energy values. In the former case the transition probability $|a_s|^2$ does not increase with the time, unless ν is equal to ν_{s0}, where $\nu_{s0} = |W_s - W_0|/h$; in this case it increases with the square of the time, as may easily be seen from (24). To obtain a result of physical significance one must assume that the perturbing field is not strictly monochromatic, but

consists of a large number of fields of different frequency in the neighbourhood of ν_{s0}, superimposed on one another. The transition probability is now obtained by integrating $|a_s|^2$ with respect to ν over the critical value ν_{s0}. We write in (22) $\lambda^2 = d\nu$. The second term in (24) clearly contributes nothing of importance (if $W_s > W_0$), and we obtain for the transition probability

$$\int \frac{2[1-\cos\{2\pi(W_s-W_0-h\nu)t/h\}]}{[W_s-W_0-h\nu]^2} |U_{s0}|^2 \, d\nu.$$

As t becomes large, the main part of the integral comes from the neighbourhood of $\nu = \nu_{s0}$. The integral reduces to†

$$4\pi^2|U_{s0}|^2 t/h^2. \tag{27}$$

The Einstein B coefficient (absorption coefficient) may be calculated in this way.‡

If the final state lies in the range of continuous energy values, we may use the method of § 2.1. Thus we consider that the perturbation acts during a finite interval of time T, where $\nu T \gg 1$, but $PT \ll 1$. Then, from (24), $|a_W(T)|^2 \, dW$ is the probability that the electron is ejected with energy between W, $W+dW$. This function has a strong maximum for $W = W_0+h\nu$. The total number of electrons ejected with all energies is

$$\int |a_W(T)|^2 \, dW = \int \frac{2[1-\cos\{2\pi(W-W_0-h\nu)T/h\}]}{[W-W_0-h\nu]^2}\lambda^2|U_{W0}|^2 \, dW. \tag{28}$$

As $\nu T \to \infty$, practically all the integral comes from the neighbourhood of $W = W_0+h\nu$, so that (28) may be replaced by§

$$4\pi^2 T|\lambda U_{W0}|^2/h, \qquad W = W_0+h\nu, \tag{29.1}$$

which is the required probability that the electron is ejected in the time T. Similarly, the number of electrons ejected into the solid angle $d\omega$ is, per unit time, from (18), (20),

$$\frac{|2\pi m}{i^2} \int \mathfrak{F}(r', \pi-\Theta)\lambda U(\mathbf{r}')\psi_0(\mathbf{r}') \, d\tau' \Bigg|_l \, d\omega. \tag{29.2}$$

† We make use of the formula

$$\int_{-\infty}^{\infty} \frac{1-\cos x}{x^2} \, dx = \pi.$$

‡ For further details the reader is referred to Frenkel, *Wave Mechanics, Elementary Theory*, p. 146.

§ N.B.—The hyperbolic wave function used in the evaluation of U_{W0} is normalized as in eq. (12) of this chapter.

Bethe† has shown how to interpret the wave function (23) without using the expedient of a perturbation that acts only in the time interval $0 < t < T$. In formula (23), if $\mathbf{r}$ be a point outside the atom, ψ_s vanishes and ψ_W may be replaced by its asymptotic form

$$\psi_W \sim 2(hv)^{-\frac{1}{4}}r^{-1}\sin(kr - \tfrac{1}{2}n\pi + \eta_n)S_n^u(\theta, \phi).$$

Using this expression for ψ_W, we shall show that, so long as $vt \gg 1$, the wave function (23) corresponds to an outgoing wave of finite amplitude for $r < vt$ and vanishing for $r > vt$.

For points $\mathbf{r}$ outside the atom, we have from (23), (24)

$$\Psi(\mathbf{r}, t) \sim \sum_{n,u} S_n^u(\theta, \phi)e^{-2\pi i(W_0 + h\nu)t/h} \int \lambda U_{Wnu,0} \frac{1 - e^{-2\pi i(W - W_0 - h\nu)t/h}}{W - W_0 - h\nu} \times$$
$$\times (kr)^{-1}N(W)\sin(kr - \tfrac{1}{2}n\pi + \eta_n)\, dW. \quad (30)$$

In this integral we make the substitution

$$2\pi(W - W_\nu)t/h = \zeta,$$

so that $k = 2\pi(2mW)^{\frac{1}{2}}/h = k_\nu + \zeta/vt + O(1/t^2).$

Here W_ν is written for $W_0 + h\nu$, k_ν for $2\pi(2mW_\nu)^{\frac{1}{2}}/h$. If vt is large, the integrand in (30) has a strong maximum for $W = W_\nu$, and (30) can be replaced by

$$\Psi \sim \sum_{n,u} N(W_\nu)S_n^u \lambda U_{W_\nu nu,0}\, e^{-2\pi i W_\nu t/h} \int \frac{1 - e^{-i\zeta}}{\zeta} \frac{\sin(kr - \tfrac{1}{2}n\pi + \eta_n)}{kr}\, d\zeta. \quad (31)$$

The integral on the right is equal to

$$(2ikr)^{-1}e^{ikr - \frac{1}{2}n\pi i + i\eta_n} \int [e^{i\zeta r/vt} - e^{i\zeta(r/vt - 1)}]\zeta^{-1}\, d\zeta -$$
$$- (2ikr)^{-1}e^{-ikr + \frac{1}{2}n\pi i - i\eta_n} \int [e^{-i\zeta r/vt} - e^{i\zeta(-r/vt - 1)}]\zeta^{-1}\, d\zeta. \quad (32)$$

Now if A, B are real numbers,

$$\int_{-\infty}^{\infty} [e^{iA\zeta} - e^{iB\zeta}]\frac{d\zeta}{\zeta} = i \int_{-\infty}^{\infty} \left[\frac{\sin A\zeta}{\zeta} - \frac{\sin B\zeta}{\zeta}\right] d\zeta,$$

which is clearly equal to 0 if A, B have the same sign, and to $2\pi i$ if they have opposite signs. Hence the second integral in (32), which represents the ingoing wave, vanishes; the first integral vanishes if $r > vt$, and is equal to $2\pi i$ if $r < vt$. Hence for (31) we may write

$$\Psi \sim (2kr)^{-1}e^{ikr - 2\pi i Wt/h}2\pi N(W)\sum_{n,u}\exp(i\eta_n - \tfrac{1}{2}n\pi i)S_n^u(\theta, \phi)\lambda U_{Wnu,0} \quad (r < vt)$$

$$\sim 0 \quad (r > vt).$$

Formulae (29.1), (29.2) for the number of electrons ejected may easily be deduced.

† *Ann. der Phys.*, **4** (1930), 443.

3.1. *Ionization of a Hydrogen Atom by a Light Wave.*

If we take for the scalar and vector potentials of the light wave

$$\Phi = \phi(x, y, z)e^{-2\pi i \nu t} + \text{complex conjugate,}$$

$$\mathbf{A} = \mathbf{a}(x, y, z)e^{-2\pi i \nu t} + \text{complex conjugate,}$$

then we have for the perturbing term the operator

$$V(\mathbf{r}, t) = U(\mathbf{r})e^{-2\pi i \nu t} + \text{complex conjugate,}$$

where $U(\mathbf{r}) = -\epsilon\phi + (\epsilon h/2\pi i m c)\mathbf{a}\cdot\text{grad}$ (Schrödinger)

$$= -\epsilon\phi - \epsilon\rho_1(\boldsymbol{\sigma}\cdot\mathbf{a})$$ (Dirac).

For a plane-polarized wave along the z-axis one may take

$$\phi = 0, \qquad a_x = ae^{iqz}, \qquad a_y = a_z = 0.$$

Hence $$U_{s0} = \frac{\epsilon h a}{2\pi i m c} \int \psi_s^* e^{iqz} \frac{\partial\psi_0}{\partial x}\, d\tau.$$

If the light wave has wave-length long compared with the radius of the atom, e^{iqz} may be replaced by unity.†

4. Transitions caused by a Perturbation which is not a Function of the Time

The formulae of the preceding section are at once applicable, by putting $\nu = 0$. Since in § 3.1 transitions were possible only to states of energy $W_0 \pm h\nu$, where W_0 is the initial energy, it follows that transitions are only now possible to states of energy W_0. Energy is therefore conserved in such transitions, as may be seen from the physical nature of the processes involved.

4.1. *Final and Initial States Unquantized.*

Scattering of a Beam of Electrons by a Centre of Force.

We make use of formula (29.2). For ψ_0 we take a beam of electrons normalized so that one electron crosses unit area per unit time, so that

$$\psi_0 = v^{-\frac{1}{2}}\exp(ik\mathbf{n}_0\cdot\mathbf{r}).$$

$U(r)$ is the potential energy of the electron in the field of the scattering centre. $\mathfrak{F}(r', \pi-\Theta)$ reduces to $\exp(-ik\mathbf{n}\cdot\mathbf{r}')$, where $\mathbf{n}$ is a unit vector in the direction θ, ϕ. Thus (29.2) reduces to

$$\left|\frac{2\pi m}{h^2} \int \exp[ik(\mathbf{n}_0-\mathbf{n})\cdot\mathbf{r}']U(\mathbf{r}')\, d\tau'\right|^2,$$

which is the formula obtained by the first approximation of Born's method [Chap. VII, eq. (5)].

† For the application of these formulae to the calculation of the photoelectric effect cf. Sommerfeld, *Wave Mechanics*, p. 177, and *Ann. der Phys.*, **4** (1930), 409; Hulme, *Proc. Roy. Soc.*, A, **133** (1931), 381; Sauter, *Ann. der Phys.*, **9** (1931), 217.

4.2. *Initial State Quantized, Final State Unquantized.*

We take for our example a non-relativistic theory of the internal conversion of γ-rays. We suppose an α-particle in the nucleus, coordinate $\mathbf{R}$, is in an excited state described by a wave function $\chi_i(\mathbf{R})$, and an electron in the atom in the normal state in the K level, described by a wave function $\psi_i(\mathbf{r})$. We require the probability per unit time that the α-particle jumps to its normal state (wave function $\chi_f(\mathbf{R})$), giving up its energy to the electron, which is thereby ejected. If

$$V(\mathbf{r}, \mathbf{R}) = -2\epsilon^2/|\mathbf{R}-\mathbf{r}|$$

be the interaction between them, then by (23) this probability is

$$\sum \frac{4\pi^2}{h} \iint d\mathbf{r}d\mathbf{R}\ \chi_f^* \psi_f^* V(\mathbf{r}, \mathbf{R})\chi_i\psi_i\ \ d\omega, \tag{33}$$

where ψ_f represents the wave function of the final state normalized as in equation (34), and the summation is over all possible final states with the requisite energy.

The escape of an α-particle from a radioactive nucleus has been treated by this method by Born.†

<p style="text-align:center">† Zeits. f. Physik, 58 (1929), 306.</p>

RELATIVISTIC TREATMENT OF THE TWO-BODY PROBLEM; INFLUENCE OF RADIATIVE FORCES ON THE SCATTERING; EMISSION OF CONTINUOUS X-RAY SPECTRUM; NUCLEAR PROBLEMS

1. Relativistic Quantum Mechanics. Use of Retarded Potentials

The work of Dirac† provides a complete relativistic theory of the motion of a single particle (proton or electron) in an electromagnetic field. Dirac's theory has been applied to the hydrogen atom,‡ to the nuclear scattering of fast electrons,§ and to the interaction of an electron with electromagnetic radiation of high frequency.‖ On the other hand, a complete relativistic theory of problems involving the interaction of two or more particles is, at present, lacking. However, there is a certain limited class of such problems which may be solved; namely, the calculation of transition probabilities under conditions such that first-order perturbation theory (first Born approximation) is valid.

In order to illustrate the method by which such transition probabilities may be calculated, we shall consider the following problem (Auger effect). In a heavy atom, a K electron has been ejected; there is therefore a finite probability that an L electron will fall into the K ring, giving up its energy either to a light quantum or to one of the other atomic electrons. We shall calculate the probability that the L electron gives up its energy to an optical electron.

The method we shall use precludes the possibility of using antisymmetrical wave functions for the initial or final states. We shall treat the electrons separately, denoting by $\mathbf{R}$ the position of the inner electron, by $\chi_i(\mathbf{R})$ the wave function of its initial state in the L ring, and by $\chi_f(\mathbf{R})$ its final state in the K ring. We denote the wave function of the initial state of the optical electron by $\psi_i(\mathbf{r})$ and the final ionized state by $\psi_f(\mathbf{r})$. The effect of the antisymmetry is considered at the end of this section.

The inner electron can return to the K level either by giving up its energy to the electron, or by emitting a quantum of radiation. The

† *Proc. Roy. Soc.*, A, **117** (1928), 618, and *Quantum Mechanics*, Chap. XIII.
‡ Darwin, *Proc. Roy. Soc.*, **118** 1928), 654; Gordon, *Zeits. f. Physik*, **48** (1928), 1.
§ Cf. Chap. IV, § 4, of this book.
‖ For the Compton effect cf. Klein and Nishina, *Zeits. f. Physik*, **52** (1929), 893; for photoelectric effect cf. Hulme, *Proc. Roy. Soc.*, A, **133** (1931), 381; Sauter, *Ann. der Phys.*, **9** (1931), 217.

probability per unit time of the latter event is denoted by $A_{i \to f}$, the Einstein A coefficient. According to any completely non-relativistic theory ($c \to \infty$) the A coefficient is zero, since in the absence of a radiation field the atom will stay in the excited state for ever. Dirac[†] has been able to account for the A coefficient by treating the radiation field as an assembly of light quanta obeying quantum-mechanical laws. Before the formulation of Dirac's theory the A coefficient was obtained in the following way.[‡]

The radiating system—in our case the L electron—is treated as a classical charge distribution, of density

$$\rho_{fi} \exp(-2\pi i \nu_{fi} t) + \text{complex conjugate}, \tag{1}$$

where
$$\rho_{fi} = -\epsilon \chi_f^* \chi_i.$$

The current vector corresponding to this charge density is

$$\mathbf{j}_{fi} \exp(-2\pi i \nu_{fi} t) + \text{complex conjugate},$$

where

$$\mathbf{j}_{fi} = \epsilon \chi_f^* \rho_1 \boldsymbol{\sigma} \chi_i, \qquad \text{(Dirac's equation)}$$

$$= \frac{\epsilon h}{4\pi i m} (\chi_f^* \operatorname{grad} \chi_i - \chi_f \operatorname{grad} \chi_i^*) \qquad \text{(Schrödinger's equation)}.$$

On the classical theory such a charge density will give rise to an oscillating electromagnetic field, radiating energy. The energy radiated per unit time may be calculated. If we divide this by the energy of a light quantum, $E_i - E_f$, we obtain a formula for the A coefficient.

It is clear that this method of calculating the A coefficient is an unsatisfactory mixture of classical and quantum mechanics; nevertheless it is along these lines that we must proceed in order to obtain a relativistic theory of the interaction of two particles. We proceed to find the field due to the oscillating charge density (1).

By classical electromagnetic theory the scalar potential Φ and vector potential $\mathbf{A}$ due to this charge density are given by the differential equations

$$\nabla^2 \Phi - \frac{1}{c^2} \frac{\partial^2 \Phi}{\partial t^2} = -4\pi \rho_{fi} \exp(-2\pi i \nu_{fi} t) + \ldots \tag{2.1}$$

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\frac{4\pi}{c} \mathbf{j}_{fi} \exp(-2\pi i \nu_{fi} t) + \ldots. \tag{2.2}$$

To obtain a particular integral we set

$$\left.\begin{aligned} \Phi &= \phi(x, y, z) \exp(-2\pi i \nu_{fi} t) \\ \mathbf{A} &= \mathbf{a}(x, y, z) \exp(-2\pi i \nu_{fi} t) \end{aligned}\right\} + \text{complex conjugate,} \tag{3}$$

† *Proc. Roy. Soc.*, A, **114** (1927), 243, and *Quantum Mechanics*, p. 218.
‡ Cf. O. Klein, *Zeits. f. Physik*, **41** (1927), 407.

and obtain $\qquad (\nabla^2 + 4\pi^2\nu_{fi}^2/c^2)\phi = -4\pi\rho_{fi}$, $\qquad\qquad$ (4)

etc. The solution, of this equation representing an outgoing wave only, is

$$\phi = \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \exp(2\pi i\nu_{fi}|\mathbf{r}-\mathbf{r}'|/c)\rho_{fi}(x',y',z')\,d\tau'. \qquad (5)$$

Taking the asymptotic form of (5), we obtain, for large r,

$$\Phi \sim r^{-1} \exp\{2\pi i\nu_{fi}(r/c-t)\} \int \exp(-2\pi i\nu_{fi}\mathbf{n}\cdot\mathbf{r}'/c)\rho_{fi}(x',y',z')\,d\tau' + ...,$$

where $\mathbf{n}$ is the vector $\mathbf{r}/r$. A similar expression is obtained for the vector potential; the rate of emission of energy may thus be calculated.

In order to obtain the probability that the L electron will give up its energy to the optical electron, we proceed as though the field Φ, $\mathbf{A}$ given by (5) were in fact present, and calculate its effect on the optical electron by the method of Chap. XIV, § 3. The probability of ejection increases with the time, only if the energy received by the electron is equal to $\pm h\nu_{fi}$. The probability per unit time is then (Chap. XIV, eq. (29.1))

$$\frac{4\pi^2}{h}\left| \int \psi_f^*\{-\epsilon\phi - \epsilon\rho_1\mathbf{a}\cdot\mathbf{\sigma}\}\psi_i\,d\tau \right|^2, \qquad (6)$$

where ψ_f is the wave function of the final state of the electron, normalized to represent one emitted electron per unit time.

If we make $c \to \infty$ in (5), we obtain

$$\phi = -\epsilon \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \chi_f^*(\mathbf{r}')\chi_i(\mathbf{r}')\,d\tau',$$

$$\mathbf{a} = 0,$$

and hence (6) reduces to the non-relativistic formula, Chap. XIV, eq. (33).

With this method of treatment it is meaningless to inquire whether the optical electron is ejected by direct interaction with the L electron, or whether a light quantum is first emitted and then re-absorbed. Both processes are included in (6).

Formula (6) takes no account of the antisymmetrical property in non-relativistic quantum mechanics. We can obtain a formula which, as $c \to \infty$, tends to the non-relativistic formula with antisymmetrical wave functions. Let us denote by $|A|^2$ the expression (6). $|A|^2$ is the probability that the L electron falls to the ground state, and the optical electron is ejected. Similarly we can find the probability $|B|^2$ that the optical electron falls to the ground state, and the L electron is ejected. The required expression is

$$|A-B|^2,$$

which is probably the correct expression for the number of electrons

ejected of both kinds. The expression must be summed over all possible final states.

Calculations on these lines for the Auger effect have not at present been carried out; this section is intended as an example of the method, rather than as a discussion of the effect for purposes of comparison with experiment.

2. Relativistic Treatment of Collision Problems

The excitation and ionization of atoms by fast electrons may be treated by the method of § 1.† We shall consider the problem of a beam of electrons incident on a hydrogen atom in the normal state, with wave function $\psi_i(\mathbf{r})\exp(-2\pi i E_i t/h)$. We require the probability that an electron is scattered in a given direction after exciting the atom to a state with wave function $\psi_f(\mathbf{r})\exp(-2\pi i E_f t/h)$.

As in § 1, the interaction between the two electrons is treated as a small perturbation. For the unperturbed wave function of the incident electrons one should take, therefore, the wave function for a stream of electrons scattered by a nucleus (Chap. III, eq. (23)). Since, however, $v \sim c$, $\epsilon^2/hv \ll 1$, so that this may be replaced by a plane wave, to the order to which we are working [neglect of $(\epsilon^2/hc)^2$, cf. § 3]. We therefore take for our zero-order wave function χ_i, a plane wave normalized to give one electron crossing unit area per unit time, so that

$$\chi_i(\mathbf{R}) = v^{-\frac{1}{2}}\exp\{2\pi i(p_i Z - Wt)/h\}.$$

For the corresponding wave function with Dirac electrons, cf. Chap. IV, eq. (12).

To obtain the probability of scattering we treat the atom as a varying charge distribution of density (cf. (1) above)

$$-\epsilon\psi_f^*(\mathbf{r})\psi_i(\mathbf{r})\exp\{2\pi i(E_f - E_i)t/h\}, \tag{7}$$

with a corresponding expression for the current; we then calculate the effect of the field of this charge on the incident beam of electrons. The method is that of Chap. XIV, § 3. The theory predicts that electrons will be scattered with energies $W - E_f + E_i$. One must *not* add the complex conjugate term to (7), for this would predict the presence of electrons scattered with energy $W - E_i + E_f$, more energy than they had initially.‡

The field due to (7) cannot be interpreted as the field radiated by

† The method is due to Møller, *Zeits. f. Physik*, **70** (1931), 786.

‡ In the case of § 1, there is no final state of energy $W_i - E_i + E_f$. Thus the presence of the conjugate term makes no difference to the number of electrons ejected.

the atom, as in § 1, firstly because the atom is initially in its normal state and is not radiating, and secondly because the field is complex.

With ϕ and $\mathbf{a}$ given by § 1, equations (3) and (4), we see from Chap. XIV, eq. (29.2), that the differential cross-section for scattering in a solid angle $d\omega$ is

$$|f(\theta)|^2 \, d\omega = v_f \, \frac{2\pi m}{h^2} \left| \int \mathfrak{F}(\mathbf{r}')[-\epsilon\phi-\epsilon\rho_1(\boldsymbol{\sigma}\cdot\mathbf{a})]\chi_i(\mathbf{r}') \, d\tau' \right|^2 d\omega, \qquad (8)$$

where $\qquad\qquad \mathfrak{F}(\mathbf{r}') = \exp(-2\pi i \mathbf{p}_f\cdot\mathbf{r}'/h) \qquad$ (Schrödinger),

$\mathbf{p}_f$, v_f being the momentum and velocity after the collision. For Dirac electrons cf. Chap. IV, eq. (12); $\mathfrak{F}$ is the complex conjugate of the wave function for an electron travelling in the direction $\mathbf{p}_f$, normalized so that there is one particle per unit volume.

In the non-relativistic theory one must use an antisymmetrical wave function to describe a collision between an electron and a hydrogen atom. In the relativistic theory discussed here no wave function for the whole system appears, but we can take account of the antisymmetry in the same way as in § 1. Thus in equation (8) we have obtained an expression $|f(\theta)|^2 \, d\omega$ for the probability that an electron will be ·scattered into the solid angle $d\omega$. If in (7) we replace $\psi_f(\mathbf{r})$ by a hyperbolic wave function describing an electron ejected with momentum p_f, and $\mathfrak{F}$ in (8) by the wave function $\psi_f(\mathbf{r})$ of an electron captured in the state f in the atom, we obtain the probability $|g(\theta)|^2 \, d\omega$ that the incident electron is captured, and the atomic electron ejected. In the non-relativistic theory, when one takes account of the antisymmetry, the probability for scattering into the solid angle $d\omega$ is

$$\sum |f(\theta)-g(\theta)|^2 \, d\omega, \qquad (9)$$

where the summation is over all possible initial and final directions of the spin (cf. Chap. V, § 6). We may assume that, in the relativistic theory also, the scattering is given by the formula (9).

Formulae for the stopping-power and primary ionization may be obtained by evaluating integrals of the type (8), and summing over all final states. (For results see below.) We must, however, remark here that all important contributions to the primary ionization are made by collisions in which the incident electron changes its momentum by a small amount only. Under these conditions the method of impact parameters is applicable. Williams† has shown that all the results given below may be deduced by this method, the incident electron being treated as a moving centre of force, with the field demanded by

† *Proc. Roy. Soc.*, **139** (1933), 163.

the 'classical' relativity theory. We conclude that an experimental test of these formulae does not provide a test of the relativistic quantum theory of the interaction of two electrons. This theory only provides formulae which can be obtained in no other way, when applied to problems where the incident particle loses a large proportion of its energy.

The formulae for the stopping-power and cross-section for ionization are,[†] in the notation of Chap. XI, §§ 3.3 and 4.2,

$$-\frac{dT}{dx} = \frac{2\pi\epsilon^4 N}{mv^2}\left\{\log\frac{2mv^2}{\alpha Rh} - \log\left(1-\frac{v^2}{c^2}\right) - \frac{v^2}{c^2}\right\}$$

$$Q_{nl}^i = \frac{2\pi\epsilon^4}{mv^2}\frac{c_{nl}\,Z_{nl}}{|E_{nl}|}\left\{\log\frac{2mv^2}{C_{nl}} - \log\left(1-\frac{v^2}{c^2}\right) - \frac{v^2}{c^2}\right\}.$$

By comparison with the corresponding formulae (68) and (50) of Chapter XI we see that the chief difference between these relativistic formulae and the non-relativistic formula is the presence in the relativistic formulae of a term $-\log(1-v^2/c^2)$. This term has the effect of producing a minimum in dT/dx and Q_{nl}^i at sufficiently high velocities. Otherwise there is no appreciable modification. Thus for electrons in air Bethe and Fermi give the following values of dT/dx:

Initial energy in volts	10^5	10^6	10^7	10^8	10^9	10^{10}
dT/dx	3·67	1·69	1·95	2·47	2·99	3·48.

3. Collision between two Free Electrons

The first application of the method of § 2 to a collision problem was made by Møller,[‡] who applied it to the collision between two free particles. Since the effect of one electron on the other is treated as a first-order perturbation, the results are of an accuracy equal to that of the first approximation in Born's method. With an inverse square law field, $V = \pm\epsilon^2/r$, the successive approximations in Born's method correspond to an expansion[§] in powers of the constant $2\pi\epsilon^2/hv$. A relativistic correction is only of interest if $v \sim c$, and thus Møller's formula neglects $2\pi\epsilon^2/hc$ in comparison with unity. An attempt to find

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† These formulae have been derived by Bethe and Fermi, *Zeits. f. Physik*, **77** (1932), 296, using Møller's method, and by E. J. Williams, loc. cit., using the method of impact parameters.

‡ *Zeits. f. Physik*, **70** (1931), 786; *Ann. der Phys.*, **14** (1932), 531.

§ If we take for our unit of length $h/2\pi mv$, Schrödinger's equation for an electron in the inverse square law field becomes

$$\nabla^2\psi + (1\pm 4\pi\epsilon^2/hvr)\psi = 0.$$

Dirac's second-order equation takes a similar form (cf. Mott, *Proc. Roy. Soc.*, A, **124** (1931), 425).

a more accurate formula cannot be made without taking into account the loss of energy by radiation, since if a particle moving with velocity comparable with c is scattered through a large angle, the probability that it will lose energy in the form of radiation is of order of magnitude† $2\pi\epsilon^2/hc$.

Møller's formula‡ for the cross-section for scattering between angles θ, $\theta+d\theta$ is

$$I(\theta)\,d\theta = 4\pi\left(\frac{\epsilon^2}{mv^2}\right)^2\frac{\gamma+1}{\gamma^2}\,dx\left\{\frac{4}{(1-x^2)^2}-\frac{3}{1-x^2}+\frac{(\gamma-1)^2}{4\gamma^2}\left[1+\frac{4}{1-x^2}\right]\right\},$$

(10)

where $\qquad x = \cos\theta^* = \dfrac{2-(\gamma+3)\sin^2\theta}{2+(\gamma-1)\sin^2\theta}, \qquad \gamma = \left(1-\dfrac{v^2}{c^2}\right)^{-\frac{1}{2}}.$

θ^* is the angle of scattering referred to axes with respect to which the centre of gravity of the two electrons is at rest. It is interesting that if one applies the method of the preceding sections, using the second-order relativistic wave equation without the spin terms, one obtains the same formula without the term

$$\frac{(\gamma-1)^2}{4\gamma^2}\left[1+\frac{4}{1-x^2}\right],$$

(11)

which may thus be considered as the contribution made by the spin.

For small angles, Møller's formula gives for the effective cross-section for loss of energy between Q, $Q+dQ$

$$\frac{2\pi\epsilon^4}{mv^2}\frac{dQ}{Q^2},$$

(12)

a result predicted by Bohr§ in 1913.

Experiments have been carried out by Champion‖ to test the formula (10). Two hundred and fifty forked β-ray tracks have been photographed in an expansion chamber, the initial values of v/c lying between 0·82 and 0·92. The agreement with the theoretical formula is good, as shown below.

	No. scattered.	
Angle.	Obs.	Møller.
30–max.	10	13
20–30	26	30
10–20	214	230

† Cf. § 4. If the two colliding particles are of equal mass and charge, the dipole moment vanishes and the probability of radiation is much less.

‡ *Ann. der Phys.*, **14** (1932), 568, eq. (74).

§ *Phil. Mag.*, **25** (1913), 10; **30** (1915), 58.   ‖ *Proc. Roy. Soc.*, A, **137** (1932), 688.

It should, however, be noticed that the 'spin' term (11) makes only a very small contribution for angles less than 30°.

On the other hand Williams and Terroux† and Williams‡ have produced evidence which shows that, for $v/c \sim 0.9$ and $Q \sim 10,000$ volts, the energy loss is about twice as great as that given by formula (12).

4. Influence of Radiative Forces on Nuclear Scattering

When an electron or proton is scattered by a nucleus, there is a finite probability that it will lose energy in the form of radiation. In order to calculate this energy loss, we must take into account the reaction between the moving particle and the radiation field. The phenomenon is the analogue, for states of positive energy, of the spontaneous emission of radiation by atoms, and the method of calculation is similar to that used to obtain the Einstein A coefficient.

Let us suppose that a beam of electrons of energy E, such that one particle crosses unit area per unit time, falls on a nucleus. Let us denote by

$$I(\theta, \phi; \alpha, \beta; \nu) \, d\omega d\Omega d\nu \qquad (13)$$

the probability that an electron will be scattered in the direction θ, ϕ into the solid angle $d\omega$ after giving up energy to a light quantum of frequency between ν and $\nu + d\nu$ and with its electric vector lying in the solid angle $d\Omega$ in the direction α, β.

From (13) we may deduce the various measurable quantities as follows. We denote by

$$d\nu d\omega \int I \, d\Omega = I_e(\nu, \theta) \qquad (14)$$

the probability that an electron will be scattered into the solid angle $d\omega$ with energy between $E - h\nu$, $E - h(\nu + d\nu)$, and by

$$d\nu d\Omega \int I \, d\omega = I_q(\nu, \alpha) \qquad (15)$$

the probability that a quantum of radiation will be emitted, with its electric vector in the solid angle $d\Omega$.

A further problem is the calculation of the correction to the Rutherford formula for elastic collisions that will be introduced by the radiative forces; this has not been investigated, but is probably not more than 5 per cent., even for fast electrons and large angles.

A formula for $I(\theta, \phi; \alpha, \beta; \nu)$ has been obtained by Mott,§ using the

† Ibid., **126** (1929), 289.   ‡ Ibid., **130** (1930), 328.
§ Mott, *Proc. Camb. Phil. Soc.*, **27** (1931), 255.

theory of spontaneous emission due to Dirac.† We introduce the following notation:

$V(r)$ is the interaction energy between the nucleus and colliding particle.

$\mathfrak{F}_E(r, \theta)$ is the solution of the equation

$$\nabla^2 \mathfrak{F} + \frac{8\pi^2 m}{h^2}(E - V)\mathfrak{F} = 0, \tag{16}$$

having asymptotic form ‡

$$\mathfrak{F} \sim e^{ikz} + r^{-1}e^{ikr}f(\theta).$$

$\mathbf{l}_{\alpha\beta}$ is a unit vector in the direction α, β; E, v, E', v' are the kinetic energy and velocity of the electron before and after the collision. Then

$$I \, dv d\Omega d\omega = \frac{v'}{v} \frac{\epsilon^2}{\pi^2 h^3 c^3} |J|^2 \frac{dv}{v} \, d\Omega d\omega, \tag{17}$$

where

$$J = \int \mathfrak{F}_{E'}(r', \pi - \Theta)\{\mathbf{l}_{\alpha\beta} \cdot \operatorname{grad} V(r')\}\mathfrak{F}_E(r', \theta') \, d\tau'$$

and

$$\cos\Theta = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi').$$

In the case of the Coulomb field, $V(r)$ is equal to $-Z\epsilon^2/r$. $\mathfrak{F}(r, \theta)$ is given by Chap. III, eq. (15).§

If $2\pi Z\epsilon^2/hv \ll 1$, approximate expressions may be obtained for J by writing

$$\mathfrak{F}(r, \theta) = e^{ikz}.$$

More accurate expressions have been obtained by Scherzer;‖ these are rather complicated, and the simpler expressions, which give the order of magnitude of the effect, are reproduced here. We have

$$I_e(\theta, v) = \left(\frac{Z\epsilon^2}{2pv}\right)^2 \frac{2\pi\epsilon^2}{hc} \frac{16}{3\pi} \frac{dv}{v}\left(\frac{p}{p'} + \frac{p'}{p} - 2\cos\theta\right)^{-1}, \tag{18}$$

where v, p, v', p' are the velocity and momentum before and after the collision.

We see from (18) that *if* an electron is scattered through an angle θ, the probability that it will emit a photon of frequency between v and $v + dv$ is

$$\frac{16}{3\pi} \frac{2\pi\epsilon^2}{hc} \frac{v^2}{c^2} \frac{\sin^4\frac{1}{2}\theta}{p/p' + p'/p - 2\cos\theta} \frac{dv}{v}. \tag{19}$$

4.1. *Relativity Correction.*

A complete relativistic theory of the effect of the radiation forces has not at present been given. However, it is extremely probable that (19) still gives the order of magnitude of the effect correctly, for the following

† *Proc. Roy. Soc.*, A, **114** (1927), 243. ‡ Cf. Chap. II, eq. (17).
§ Denoted there by $\psi(r, \theta)$. ‖ *Ann. der Phys.*, **13** (1932), 137.

reasons: Formula (17) takes account only of dipole radiation, but since the minimum wave-length of the emitted radiation is always long compared with the classical distance of closest approach, it is unnecessary to consider quadripole radiation. If one carries through the calculation described above with, instead of (16), the relativistic wave equation without spin, namely,

$$\nabla^2\psi + \left\{ m^2c^2 - \left(\frac{E}{c} - \frac{Z\epsilon^2}{cr}\right)^2 \right\}\psi = 0,$$

one obtains for $I(\theta, \nu)$ exactly the formula (18). It is unlikely that the spin terms will make much difference. The number of scattered electrons, neglecting spin corrections, is (Chap. IV, § 4)

$$(Z\epsilon^2/2pv)^2 \operatorname{cosec}^4\tfrac{1}{2}\theta. \tag{20}$$

Dividing, one obtains (19). It is not therefore likely that radiative forces have a large effect on the scattering, even for very fast electrons, owing to the small factor $2\pi\epsilon^2/hc$ in (19).

We note, however, that formulae (18) and (19) are certainly not valid for very small ν, because they give an infinite number of electrons scattered into a given solid angle. This is probably due to a breakdown in the perturbation method used in solving the equation giving the interaction between the radiation field and the electron.†

4.2. *Continuous X-radiation.*

By integrating (13) over all directions of the scattered electrons, one may investigate the spectrum of the radiation emitted when cathode rays fall on a *thin* target. The approximation used above leads to wrong results except for very light elements ($Z \sim 2$). The exact formula has been investigated by Gaunt,‡ Oppenheimer,§ Sugiura,‖ and most completely by Sommerfeld,†† and good agreement with experiment has been obtained.

5. Nuclear Problems

5.1. *Anomalous Scattering.*

As shown in Chapter III, quantum mechanics leads in general to the same formulae as classical mechanics for the scattering of α-particles by nuclei, if the inverse square law of force be assumed. Anomalies arise if the incident particle has the same charge and mass as the struck particles, as shown in Chap. V, § 4. However, deviations from classical

† Cf. Mott, loc. cit.
§ *Zeits. f. Physik*, **55** (1929), 513.
†† *Ann. der Phys.*, **5** (1931), 255.

‡ *Phil. Trans. Roy. Soc.*, **229** (1930), 163.
‖ *Phys. Rev.*, **34** (1929), 858.

scattering have been observed† for several elements other than helium, and these, as well as the deviations in helium for fast α-particles, must be ascribed to the breakdown at small distances of the inverse square law of force between the nucleus and α-particle.

It is natural to attempt an explanation of the anomalous scattering by assuming that the law of force between a nucleus and an α-particle
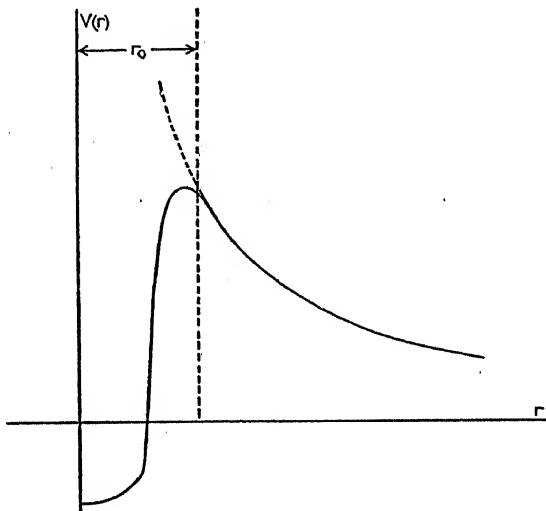
FIG. 52

is of the type introduced by Gamow, and by Gurney and Condon, to account for radioactive decay. We therefore assume that the potential energy $V(r)$ of an α-particle in the field of a nucleus is of the form illustrated in Fig. 52, where

$$V(r) = 2Z\epsilon^2/r \qquad (r > r_0),$$

and $V(r)$ is given by some other function for $r < r_0$. It must be emphasized that the form of $V(r)$ for $r < r_0$ must not be taken too seriously. It is possible that the idea of potential energy is not applicable to the problem, since the nucleus may be polarized by the field

† The anomalous scattering of α-particles has been observed by Rutherford (*Phil. Mag.*, **37** (1919), 537) and by Chadwick and Bieler (*Phil. Mag.*, **42** (1921), 923) in hydrogen; by Rutherford and Chadwick (*Phil. Mag.*, **4** (1927), 605), Chadwick (*Proc. Roy. Soc.*, A, **128** (1930), 114), and Wright (*Proc. Roy. Soc.*, A, **137** (1932), 677) in helium; by Bieler (*Proc. Roy. Soc.*, A, **105** (1924), 434) and Chadwick (*Phil. Mag.*, **50** (1925), 889) in aluminium and magnesium; by Rietzler (*Proc. Roy. Soc.*, A, **124** (1931), 154) in aluminium, beryllium, boron, and carbon; and by Duncanson and Miller in aluminium (*Proc. Roy. Soc.*, A, in course of publication).

of the incident particle, so that V is a function of the velocity. It is quite possible that quantum mechanics is not applicable within the nucleus. At the same time, we can account for a great many features of the anomalous scattering if we assume only that the α-particle, for $r > r_0$, is described by a wave function ψ satisfying Schrödinger's equation, and that for $r < r_0$ there is some quite unspecified attractive field. In view of the success of the Gamow-Gurney-Condon theory, we are here on fairly safe ground.

Details of the scattering by such a field have been worked out,[†] using the methods of Chapters II and III. We denote by R the ratio of the observed number of scattered particles to the number of particles expected according to the classical theory, and by θ the angle of scattering with reference to axes moving with the centre of gravity of the two particles. Then we obtain

$$R = \left| 1 + i\alpha^{-1}\sin^2\tfrac{1}{2}\theta \, e^{i\alpha\log\sin^2\frac{1}{2}\theta} \sum_{n=0}^{\infty}(2n+1)e^{2i(\eta_n-\eta_0)}(e^{2i\zeta_n}-1)P_n(\cos\theta) \right|^2, \quad (21)$$

where $\quad \alpha = 4\pi Z\epsilon^2/hv, \qquad e^{2i\eta_n} = \Gamma(n+1+i\alpha)/\Gamma(n+1-i\alpha).$

The quantities ζ_n are defined in the following way: if $V(r)$ is the nuclear field illustrated in Fig. 52, the solution L_n of the equation

$$\frac{d^2L}{dr^2} + \left[\frac{8\pi^2 m^*}{h^2}\{E-V\} - \frac{n(n+1)}{r^2}\right]L = 0, \qquad m^* = \frac{m_1 m_2}{m_1+m_2},$$

which vanishes at the origin, will have asymptotic form

$$L_n \sim \sin(kr - \tfrac{1}{2}n\pi - \alpha\log 2kr + \eta_n + \zeta_n).$$

The quantities ζ_n thus represent the deviation of the wave function at infinity from the form which it would have with the pure Coulomb field, and play a similar role in the theory of anomalous scattering to that of the phase constants η_n in Faxén and Holtsmark's theory of the scattering of electrons by the fields of neutral atoms. In the first case we are dealing with the deviations of the wave function from the form it would have in the Coulomb field, while in the last case we are concerned with deviations from the plane wave form.

If the ζ_n are all small they may be calculated[‡] by a perturbation method analogous to Born's but differing from it in that the unperturbed wave functions are the functions L_n instead of the corresponding

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† Mott, *Proc. Roy. Soc.*, A, **133** (1931), 228; Taylor, *Proc. Roy. Soc.*, A, **134** (1931), 103, and **136** (1932), 605. The scattering has been investigated by many authors, using the approximate method of Born (Chap. VII). However, it is easy to see that the conditions for the validity of this method are not satisfied, and that the results obtained are not even qualitatively correct.

‡ Massey, *Proc. Roy. Soc.*, A, **137** (1932), 447.

plane wave functions. Also, by following an argument similar to that of Chap. II, § 2, it can be shown that the ζ_n are all negligible† if the incident α-particles are so slow that none will enter the region $(r < r_0)$ where the Coulomb field fails. The condition that, for a given n, ζ_n should *not* be negligible is that a particle moving classically with angular momentum $[n(n+1)]^{\frac{1}{2}}h/2\pi$, impact parameter $[n(n+1)]^{\frac{1}{2}}h/2\pi mv$, should penetrate the region $r < r_0$.

Thus for sufficiently small v, R is unity, and for increasing v the terms in the series (21) become appreciable one after the other. We note that the velocity at which anomalous scattering begins is the same for all angles, in contradistinction to the classical theory. At small angles the anomalies will, however, be small, owing to the term $\sin^2\frac{1}{2}\theta$ in (21).

5.11. *Comparison with Experiment.* For elements heavier than helium, several terms of the series (21) will be required, and the experimental material is too meagre to allow of any comparison with the theory, except as to the order of magnitude of the effect. For hydrogen, however, an α-particle with angular momentum $\sqrt{2}h/2\pi$ and velocity 2×10^9 cm. sec. approaches only to a distance $6\cdot4 \times 10^{-13}$ cm. from the centre of the nucleus, which is considerably greater than the probable distance at which Coulomb forces break down. Thus only one term of the series (21) is required, and we have

$$R = |e^{-i\alpha \log \sin^2\frac{1}{2}\theta} + i\alpha^{-1}\sin^2\frac{1}{2}\theta(e^{2i\zeta_0}-1)|^2. \tag{22}$$

The formula (22) only contains one unknown parameter ζ_0, which is a function of v but not of θ. Thus from the observed scattering at constant angle, ζ_0 may be determined, and hence the scattering at all other angles may be deduced. Calculations on these lines have been carried out by H. M. Taylor,‡ and very good agreement with experiment obtained. Similar calculations for helium yield fair agreement.

5.2. *Resonance Levels.*

It was first pointed out by Gurney§ that with a field such as that illustrated in Fig. 52 there may exist narrow ranges of energy such that α-particles with energies lying in these ranges may pass easily into the nucleus, although the classical distance of closest approach is greater than r_0. The phenomenon has been discussed from a theoretical point of view by several authors; we shall summarize the results obtained.

The breadth ΔE of the level is given by the formula

$$\Delta E \sim h\lambda,$$

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† This is not the case if there is a resonance level.
‡ *Proc. Roy. Soc.*, A, **136** (1932), 605.   § *Nature*, **123** (1929), 565.

where λ is the decay constant from the level considered. λ may be calculated from a formula given by Gamow.[†]

If no disintegration of the nucleus is possible, the only result of the level will be to cause anomalous scattering for incident α-particles having their energies in the range ΔE.

If the energetic relations are such that disintegration is possible, protons will be emitted when the nucleus is bombarded by α-particles having their energies in the range ΔE. No protons will be emitted for α-particles of greater or less energy, unless the α-particles have enough energy to pass over the top of the potential barrier.

One may give an upper bound to the cross-section for disintegration; this is[‡]

$$(2n+1)h^2/4\pi m^2 v^2 \qquad (m = \text{mass of } \alpha\text{-particle}),$$

where n is the azimuthal quantum number associated with the level. In most experimental investigations, inhomogeneous beams of α-particles are used, and in that case it can be shown that the presence of resonance levels will not result in any greatly increased yield of disintegration-products.[§] This is due to the fact that the small width of the resonance level just compensates for the large probability of penetration.

The experimental evidence at present available[||] seems to indicate the existence of resonance levels; but it is doubtful whether the observed widths agree with those expected theoretically.[††]

[†] *Atomic Nuclei and Radioactivity*, p. 50.
[‡] Mott, loc. cit.
[§] Kallmann, *Naturwiss.*, **20** (1932), 393.
[||] See, for example, Chadwick and Constable, *Proc. Roy. Soc.*, A, **135** (1932), 48.
[††] Mott, loc. cit.

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